UNIVERSITY OF ILLINOIS BULLETIN

ISSUED WEEKLY

Vol. XXV JUNE 5, 1928 No. 40

[Entered as second-class matter December 11, 1912, at the post office at Urbana, Illinois, under the Act of August 24, 1912. Acceptance for mailing at the special rate of postage provided for in section 1103, Act of October 3, 1917, authorized July 31, 1918.]

EMBRITTLEMENT OF BOILER PLATE

BY

SAMUEL W. PARR

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BULLETIN No. 177

ENGINEERING EXPERIMENT STATION

PUBLISHED BY THE UNIVERSITY OF ILLINOIS, URBANA

PRICE: FORTY CENTS

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UNIVERSITY OF ILLINOIS PRESS

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EMBRITTLEMENT OF BOILER PLATE

I. Introduction

1. *Introduction.*—The first investigation of the embrittlement of boiler steel was undertaken in 1912 at the suggestion of Mr. W. L. Abbott, at that time President of the Board of Trustees of the University of Illinois. The results of this investigation were published in Engineering Experiment Station Bulletin No. 94, entitled "The Embrittling Action of Sodium Hydroxide on Soft Steel," issued in 1917. These studies were resumed in 1924 in coöperation with the Utilities Research Committee representing the Commonwealth Edison Company, the Public Service Company of Northern Illinois, the Peoples Gas, Light and Coke Company, the Middle West Utilities Company, the Chicago Rapid Transit Company, and the North Shore Electric Railway. In June, 1926, the results of the first 18 months' investigation were assembled and published in Engineering Experiment Station Bulletin No. 155, entitled "The Cause and Prevention of Embrittlement of Boiler Plate." The present bulletin, while primarily intended as a record of data secured since the publication of Bulletin No. 155, constitutes also a résumé of the entire three years' work on embrittlement.

2. *Advisory Committee.*—Mr. W. L. Abbott, Chief Operating Engineer of the Commonwealth Edison Company, was chairman, and Mr. Harry B. Gear, Assistant to the Vice-president of the Commonwealth Edison Company, was secretary of the Utilities Research Committee. The members of the sub-committee in direct charge of the investigation of the embrittlement of boiler steel were Mr. Alexander D. Bailey, Superintendent of Generating Stations, Commonwealth Edison Company, Chairman; Mr. Andrew J. Authenreith, Vice-president, Middle West Utilities Company; Mr. Arthur E. Grunert, Combustion Engineer, Commonwealth Edison Company; Mr. Robert B. Harper, Chief Testing Engineer, Peoples Gas, Light and Coke Company; Mr. John M. Lee, Construction Superintendent, Public Service Company of Northern Illinois; Mr. Emanuel Mandel, Chemist, Commonwealth Edison Company.

3. *Outline of Investigation.*—The work performed in connection with the investigation of embrittlement consisted of (a) the collection of information concerning failures apparently due to this cause from boiler manufacturers, boiler users, and the steam boiler insurance

companies; and (b) conducting tests either in the laboratory or at plants under the direct supervision of the investigation.

4. *Acknowledgment.*—Acknowledgment is made of the generous assistance and coöperation received from boiler makers, insurance inspectors, and boiler users. By maintaining a strictly neutral and unbiased relation to all interests concerned, and by omitting specific reference to the sources of information except where permission is given to do otherwise, the authors have been accorded every facility and help in pursuing these studies. Full recognition is here given and it is their desire gratefully to acknowledge this help.

This investigation has been carried on as a part of the work of the Engineering Experiment Station, of which DEAN M. S. KETCHUM is the Director; and is one of the researches in Applied Chemistry which are carried on under the direction of Professor D. B. KEYES, Professor of Industrial Chemistry.

II. HISTORY OF STUDY OF EMBRITTLEMENT

5. *Development of Study of Embrittlement.*—It should be noted at the outset that, while the phenomenon of embrittlement is not new, there has been without question an increase in the number of cases where this distress has appeared. This has been a logical sequence of the present day trend toward higher efficiencies, calling for higher pressures, and cleaner surfaces, with a resulting impetus given to methods of water purification. Doubtless also, a better comprehension and diagnosis of the difficulty has resulted in a seeming increase in the number of cases of embrittlement.

The historical development of the study of the phenomenon of embrittlement would undoubtedly show that many cases of boiler failure from embrittlement were laid to other causes in years gone by. The first indication the industry had that this type of failure was different from any previously encountered was in 1895, when a case of cracking in steam boiler drums which had been installed in 1893 occurred at a plant at DeKalb, Illinois. At that time it was suggested that the feed water might have been the cause, but little attention was paid to the suggestion.

In 1911 a plant manufacturing caustic soda reported having difficulty in the form of cracking in the seams of the boilers. This plant used as part of its supply a water which was treated with soda ash and caustic, the sodium hydroxide content in the boiler water being as high as 100 grains per gallon.

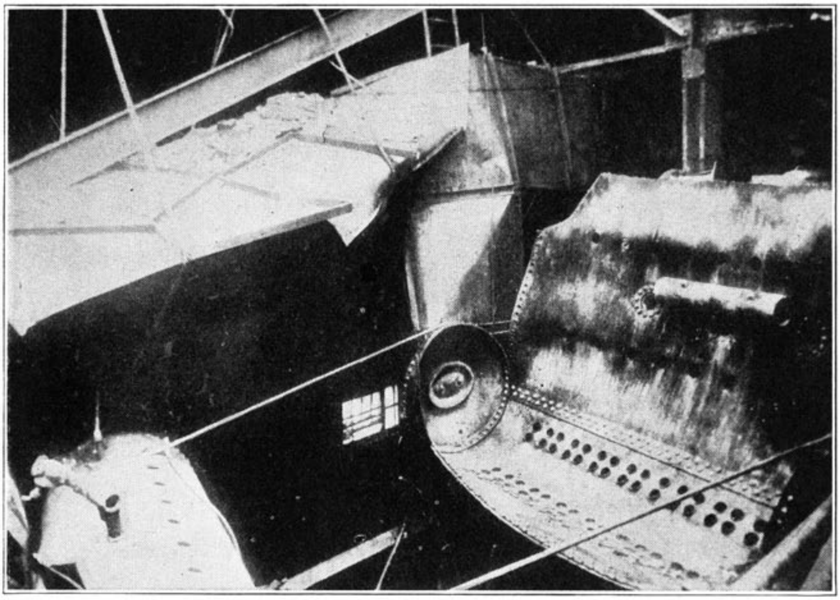

FIG. 1. BOILER EXPLODED AT BLOOMINGTON, ILLINOIS

In 1906 one of the authors of the present bulletin described an unusual type of water and outlined an area where it occurred, having Champaign-Urbana as a center, and extending west as far as Bloomington, Illinois, and east as far as Veedersburg, Indiana.* This water was characterized by the presence of free sodium bicarbonate and the almost complete absence of sodium sulphate.

It was not until 1912, when a boiler operating on this unusual type of feed water exploded at Bloomington, Illinois (see Fig. 1), suggesting a possible connection between the failure and feed water employed, that much attention was paid to this particular type of difficulty.

In 1915 two boilers in the new power plant at the University of Illinois failed and had to be replaced after less than four years of service. The University instigated an investigation which resulted in the publishing of Engineering Experiment Station Bulletin No. 94. The fact that the fracture resembled that of brittle metal more than that of a perfectly ductile plate, as shown in Figs. 2 and 3, led to the use of the term "embrittlement" as descriptive of the condition the

*Parr, S. W., "The Service Waters of a Railway System," Jour. Amer. Chem. Soc., 640-646, 1906.

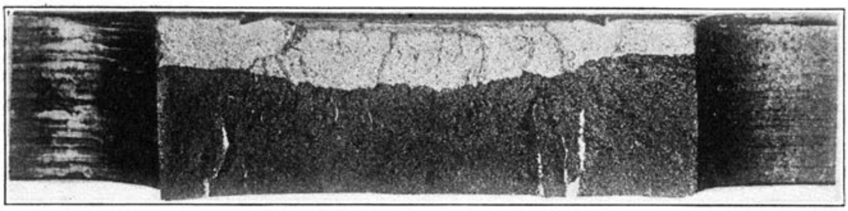

Fig. 2. Embrittled Plate Showing Nature of Cracking

plate had acquired. This investigation demonstrated the fact that the sodium·bicarbonate in the feed water hydrolized to caustic soda, and that concentrated caustic solutions weakened steel. The main thing accomplished was that an apparent relation was shown to exist between this method of failure and alkaline feed waters. At the same time a remedy was not only suggested but was put in operation in the University of Illinois power plant.

During the interval between 1916 and 1924 a considerable amount of investigation was undertaken in the effort to explain the cause of embrittlement failures, which were continuing to increase in number. The research conducted by the Babcock & Wilcox Company did much toward explaining the difficulty and bringing the issue before the boiler user. On the other hand, any suggestion that alkaline waters might have been a contributing agent was naturally opposed by water treating companies, whose treatments produced alkaline waters. Following the publication of Bulletin No. 94 users of boilers operating on alkaline water were warned by certain manufacturers to treat the feed water so as to maintain a certain sulphate to carbonate ratio. In some instances this required acid treatment, and after installing some acid treating systems the Public Utility Interests requested the University of Illinois to conduct an investigation to determine the cause of embrittlement and methods to be used to prevent it.

III. Information Obtained from Outside Sources

6. *Nature of Cracking Due to Embrittlement.*—A list of some 300 cracked boilers from plants encountering difficulty in the form of embrittlement was given in Appendix B of Bulletin No. 155. Only a brief description of the location and type of cracking observed in these cases will be given here.

An examination of these instances of embrittlement failure shows that:

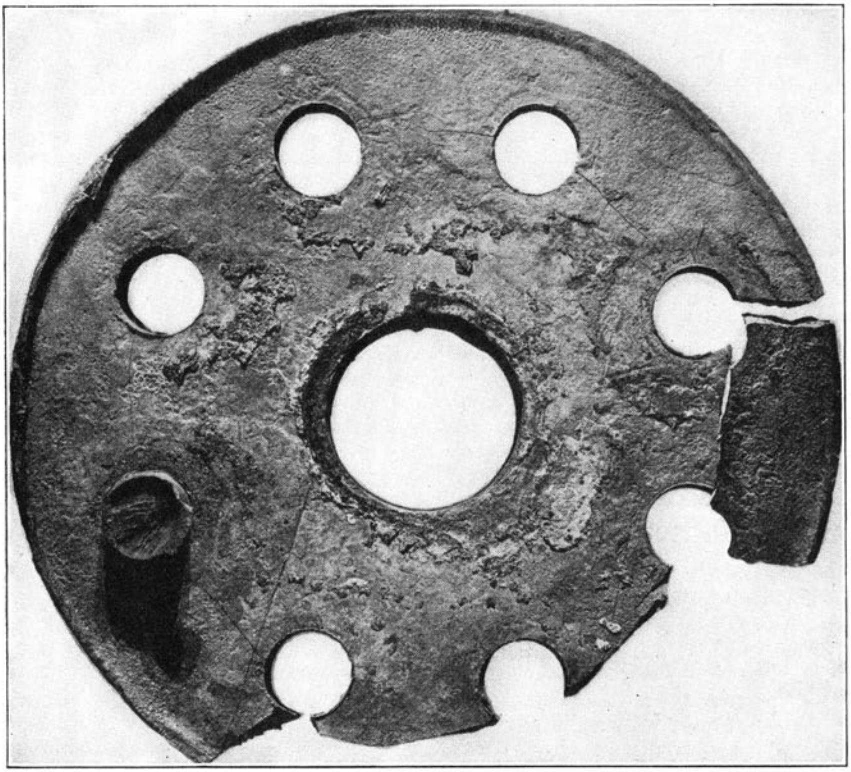

FIG. 3. EMBRITTLED BLOW-OFF FLANGE FROM BOILER USING EXCESSIVE SODA ASH TREATMENT

(1) The cracks occur primarily below the water level.

(2) The cracked plates have always been in tension and the cracks occur at points of high localized stresses.

(3) Cracks have occurred in seams having factors of safety as high as 10.

(4) The cracking is not confined to poor steel, but occurs in steel of excellent quality, as well as in steel of inferior grade.

(5) Cracking has occurred in seams of boilers built as late as 1924, with the seams made in the best manner possible at that time.

(6) Cracking has occurred with both outside calked seams, and with seams calked both outside and inside.

The characteristics of these embrittlement cracks may be summarized as follows:

TABLE 1

CHEMICAL ANALYSES OF STEEL FROM EMBRITTLED BOILERS

Location of Power Plant	Carbon per cent	Manganese per cent	Phosphorus per cent	Sulphur per cent
Buffalo, New York	0.18	0.33	0.020	0.040
Lawton, Oklahoma	0.23	0.38	0.010	0.040
Erie, Pennsylvania	0.26	0.34	0.014	0.021
Waukegan, Illinois	0.31	0.38	0.014	0.022
Steamship	0.31	0.41	0.031	0.023
Bloomington, Illinois	0.17	0.26	0.015	0.046
Hartland, Illinois	0.22	0.39	0.017	0.024
Champaign, Illinois	0.20	0.50	0.005	0.024
Los Angeles, California	0.22	0.54	0.013	0.036
Houston, Texas	0.26	0.34	0.014	0.025
Railway	0.14	0.37	0.018	0.018

(1) They do not follow the line of what is generally considered the line of maximum stress.

(2) They start on the dry side of the plate.

(3) They run in general from one rivet hole to another, though they often run past each other, leaving islands of plate.

(4) They are irregular in direction.

(5) They never extend into the body of the plate beyond the lap of the seam.

(6) There is no elongation of the plate.

(7) Rivet heads crack off or are easily dislodged.

(8) A microscopic examination of all the cracked plates reveals the fact that the crack progresses around the grain boundaries or is intercrystalline.

7. *Feed Water Conditions Observed in Cases of Embrittlement.*—A summary of the chemical conditions which characterize the feed water used in the boilers where embrittlement has occurred is as follows:

(1) Sodium carbonate is the one substance which is invariably present in the feed water.

(2) Sulphate hardness is usually absent or low in respect to the sodium carbonate present. Sodium sulphate is similarly lower than the sodium carbonate.

In the boilers in which this trouble was encountered waters having characteristics noted under (1) and (2) were used, and as a consequence of the chemical reaction in the boiler a caustic condition was developed, with sodium hydroxide in material excess over the sodium sulphate.

TABLE 2

PHYSICAL PROPERTIES OF STEEL FROM EMBRITTLED BOILERS

Location of Power Plant	Yield Point	Ultimate Strength	Reduction of Area per cent
	lb. per sq. in.		
Houston, Texas	39 160	63 800	49.4
Erie, Pennsylvania	47 100	59 800	57.1
Waukegan, Illinois	33 400	65 400	59.
Excursion Steamship		63 500	59.
Railroad	37 000	54 700	59.8
Los Angeles, California	40 100	58 800	61.4

8. *Recent Instances of Embrittlement.*—During the interval between June, 1926 and September, 1927, ten new instances of embrittlement, involving some 25 different boilers, were brought to the attention of the investigators. A rough compilation as to the cost of replacing or repairing these boilers showed that at least $150 000 was involved. In addition to the cost the fact must also be considered that in many plants the cracking had progressed so far that the lives of the operators were endangered.

These cases of embrittlement occurred on boilers operating with pressures as low as 30 lb. per sq. in. and as high as 250 lb. per sq. in., and on different types of boilers, thus illustrating further that the trouble is not confined to any one make or design of boiler. The cracks were found only in riveted areas, but occurred at random in practically any seam below the water line. Samples of steel from a large number of these cracked boilers were analyzed and tested and no marked deviation from the original mill reports was evident. This tended to confirm the opinion previously stated that embrittlement is not confined to poor steel.

In every instance the boiler feed water failed to meet the A. S. M. E. recommendation as to sodium carbonate-sodium sulphate ratio. The sulphates were low in all cases.

In one instance the embrittlement resulted from the use of a natural water having a high sodium carbonate content with the sulphate low. Two plants were using the lime-soda treatment on low sulphate waters and were over-treating with soda ash. Seven plants were using zeolite treated water. The untreated waters were low in

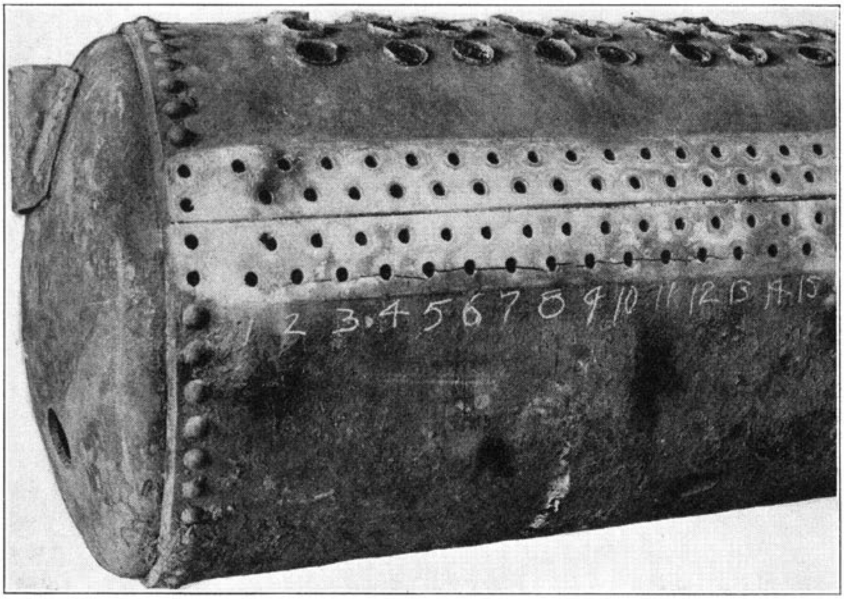

FIG. 4. EMBRITTLED DRUM FROM CHAMPAIGN, ILLINOIS
Natural sodium carbonate well water was used.

sulphate hardness and high in carbonate hardness, thus giving a water in which the sodium carbonate predominated over the sulphate. The figures show that 10 per cent of the cases of embrittlement occurred with natural waters, 20 per cent with waters treated with soda ash, and 70 per cent with zeolite-treated waters.

A brief review of the instances of failure is given below.

Case No. 1. An electric power plant supplying power and light to a city used untreated river water for 25 to 30 years without any trouble. In 1922 some new boilers were added to the installation, the older ones being still retained in service. The operating pressure was from 200 to 250 lb. per sq. in. A zeolite water softener was also installed in 1922. In 1927 it was found that cracks had developed in four boilers, both old and new boilers being affected.

Case No. 2. Two boilers installed in 1922, operating at a pressure of 250 lb. per sq. in., were found to be cracked in 1927. The water supply was city service river water, zeolite treated.

Case No. 3. Boilers operated at a pressure of 200 lb. per sq. in. using untreated Lake Michigan water for three years without trouble.

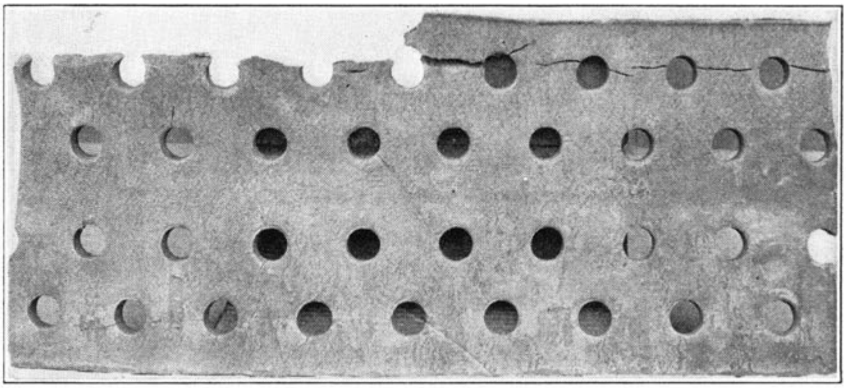

FIG. 5. EMBRITTLED STRAP FROM BUFFALO, NEW YORK
Plant used zeolite-treated lake water.

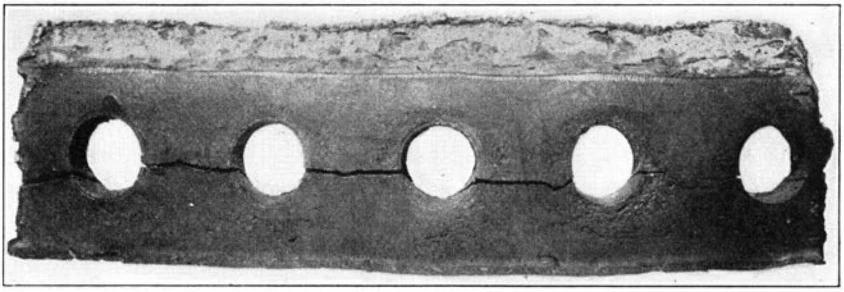

FIG. 6. EMBRITTLED SECTION FROM HEATING BOILER OPERATED AT PRESSURE OF 30 LB. PER SQ. IN.
Plant used zeolite-treated well water.

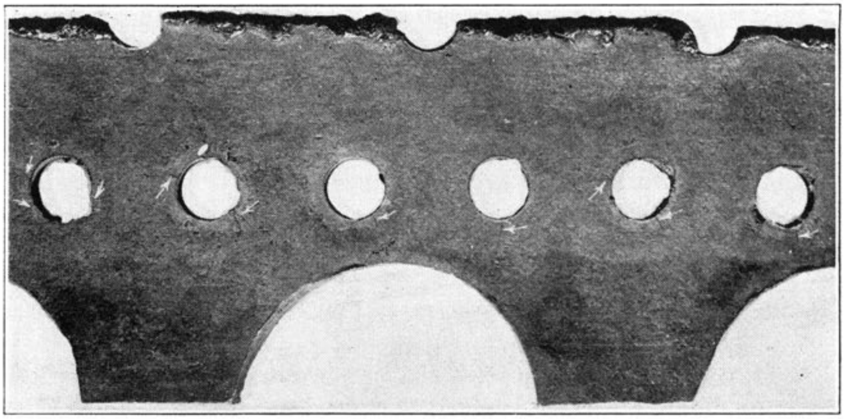

FIG. 7. EMBRITTLED PLATE FROM CALIFORNIA
Water high in sodium carbonate content was used in the boiler.

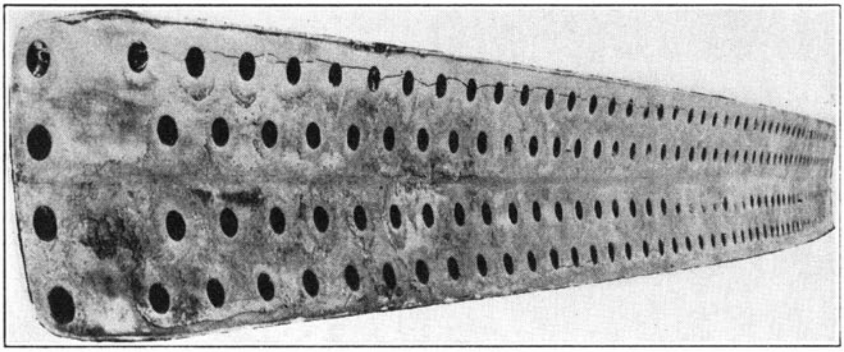

FIG. 8. EMBRITTLED BUTT STRAP FROM WISCONSIN
Zeolite-treated river water was used in the boiler.

A zeolite water softener was then installed, and 20 months later cracks were found to have developed.

Case No. 4. The boilers of a steam plant operated for several years at a steam pressure of 150 lb. per sq. in. using untreated river water without trouble. Zeolite water treatment was then introduced, and two years later trouble from cracking was experienced. Boiler No. 1, built in 1914, gave no trouble until the winter of 1926, when a circumferential crack developed on a line of rivets, extending for about one-third the circumference of the boiler. This was repaired by cutting out the damaged portion all the way around the boiler and replacing it with a new plate about a foot or so wide, making two seams. About nine months later the new rivet heads became embrittled and cracked off. Boiler No. 2, installed in 1909, developed a crack in a horizontal lap-jointed seam early in 1927. Boiler No. 5, installed in 1920, developed a crack in a horizontal butt-jointed seam during the summer of 1927.

Case No. 5. Four heating boilers operating at a pressure of about 30 lb. per sq. in. using zeolite-treated well water developed extensive embrittlement cracking after having been in service under these conditions for less than four years.

Case No. 6. A boiler seven years old, operating at a pressure of 150 lb. per sq. in., used zeolite-treated well water for three years, and developed a cracked horizontal seam.

Case No. 7. In a heating boiler five years old, operating at a pressure of 70 lb. per sq. in., using zeolite-treated well water, the rivets became embrittled and rivet heads cracked off.

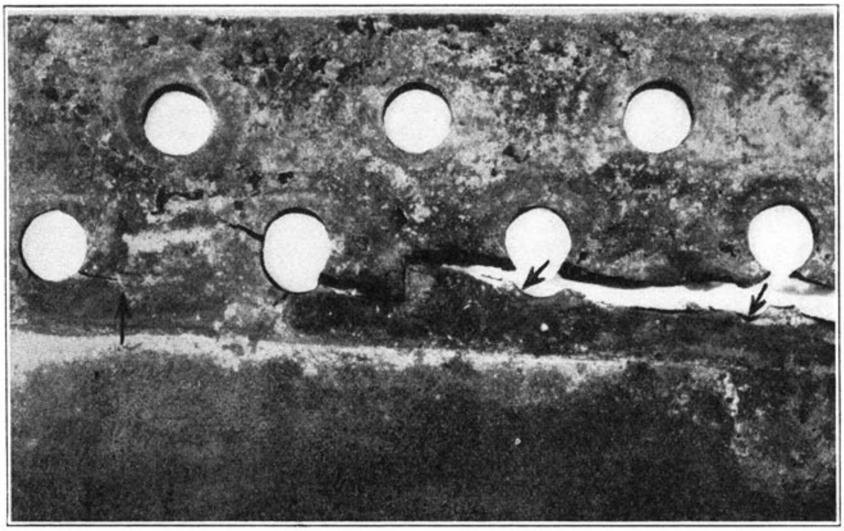

FIG. 9. SECTION OF RUPTURED PLATE WHICH FAILED DUE TO EMBRITTLEMENT
Zeolite-treated river water was used in the boiler.

Case No. 8. Boilers operating at a pressure of 150 lb. per sq. in. used untreated well water until 1913, and the same water treated with soda ash softener subsequently. The water was low in sulphate. Two drums were afterwards found to be cracked.

Case No. 9. Boilers ten years old operating at a pressure of 265 lb. per sq. in. used Lake Erie water treated by the lime-soda process, and over-treated with soda ash. One boiler developed cracks.

Case No. 10. The boilers of an excursion boat were operated about two years at a pressure of 225 lb. per sq. in., using well water high in sodium carbonate content. Four boilers developed cracking.

9. *A. S. M. E. Code.*—In 1926 the American Society of Mechanical Engineers in their Boiler Constructor Code made the following statement:

"The attention of the committee has been called to the following exceptional cases in rivet-joint cracks described as intercrystalline in character and under the water level only:

(a) boilers in certain localities fed with well water containing sodium bicarbonate, but not an appreciable quantity of sodium sulphate (similar cracking has not been reported in the same localities in boilers fed with surface water free from sodium carbonate or containing sodium sulphate equal to or exceeding the sodium bicarbonate); (b) boilers fed with water in part composed of condensate from leaky caustic evaporators; (c) boilers fed with sea water distillate

to which compounds were added resulting in high concentrations of sodium alkalinity.

In view of the particular cases of embrittlement cited above and pending further research, the maintenance of not less than the following ratios of sodium sulphate to the soda (methyl orange) alkalinity is recommended as a precautionary measure:

Working Pressure of boiler lb. gage	Relation of Sodium Carbonate Alkalinity	to	Sodium Sulphate
0 to 150	1	to	1
150 to 250	1	to	2
250 to over	1	to	3

Cracks of this particular character have not been reported in cases where water softening equipment has been intelligently used, maintaining close control over boiler concentrations and the boilers have been properly operated.*

Pending further operating data from boilers in service, it is recommended that the requirements of Par. 1-44 of Section VI of the Code be extended to all riveted seams and that careful examination of all seams be made if leaks occur and do not remain tight after proper calking."

10. *Possible Causes of Failure.*—In assembling the informational data it was realized that four factors must be considered in trying to explain the cause of these failures, namely, material, workmanship, conditions of operation, and nature of feed water used. A brief discussion of these various factors follows.

Material

Chemical analyses made of cracked plates taken from embrittled boilers are given in Table 1. These analyses do not show any marked deviation from the standard boiler plate. These plates were from boilers made during the interval between 1905 and 1924 and represent the standard boiler plate made during the last twenty years.

Table 2 gives the results of physical tests made on plates from the embrittled boilers. The test specimens were taken between the rivet holes and in some cases within an eighth of an inch of a crack. These showed no marked deviation from the specification requirements for flange steel. In addition, samples were cut from embrittled seams and tested in the laboratory in order to study their resistance to caustic attack. These samples proved to be no more susceptible to embrittlement than standard specimens made from standard flange steel.

Microscopic examination revealed that, with very few exceptions, the steel had good crystal structure, with the carbon well distributed in

*The instances of embrittlement encountered during the last year indicate that this paragraph should be modified so as to include control over sulphate-carbonate ratio.

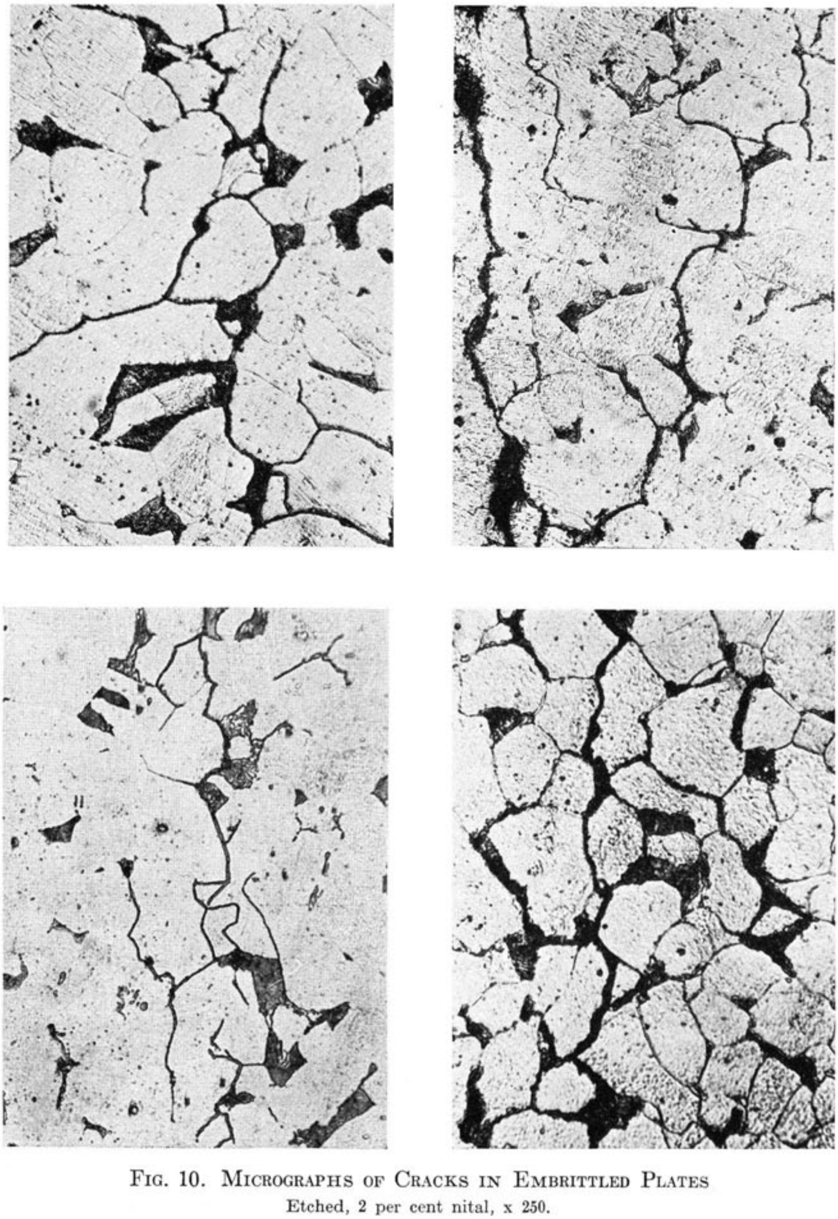

Fig. 10. Micrographs of Cracks in Embrittled Plates
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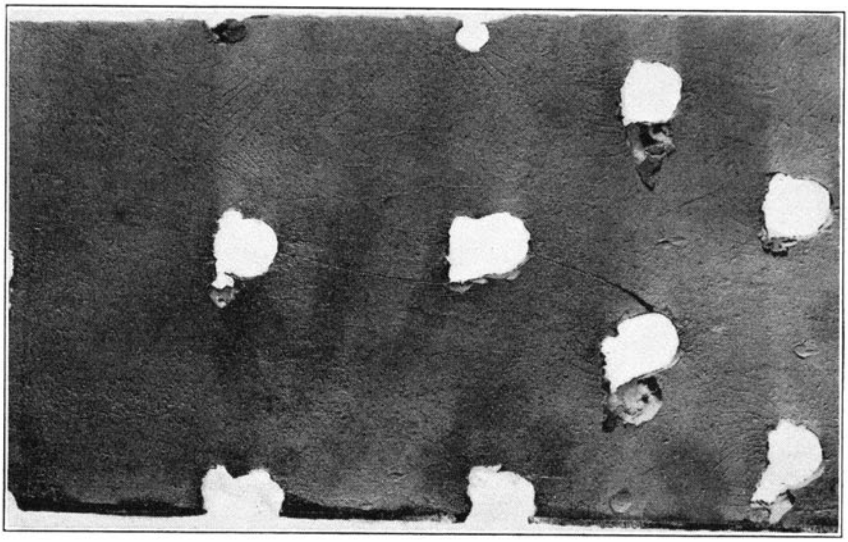

Fig. 11. Fire Side of Crown Sheet from Locomotive Showing Strain Lines Around Staybolt Holes

even-grained pearlitic form. No indications of excessive cold work were present in the majority of cases. The cracks progressed around the grain boundaries.

Figures 4 to 9, inclusive, show examples of embrittled plates. Figure 10 shows micrographs of cracks from these plates, illustrating the intercrystalline nature of the cracks. Figure 11 shows a crown plate from a locomotive with cracks running from staybolt to staybolt; Fig. 12 shows the water side of the same plate. The micrographs of these cracks show clearly that they are not intercrystalline (see Fig. 13). Figures 11 and 12 indicate the presence of strain lines around the holes and show how corrosion has been accelerated at these points of stress until the plate has cracked. Particular attention should be paid to the fact that the presence of strain configurations even when followed by cracking does not of necessity indicate that embrittlement cracking has occurred. The reverse is usually the case—no indications of strain configurations are present in the embrittled area and active corrosion is hardly ever noticeable.

Workmanship

The question of workmanship is always open to debate. No boiler is made with absolutely leak-proof, perfectly fitting seams free from

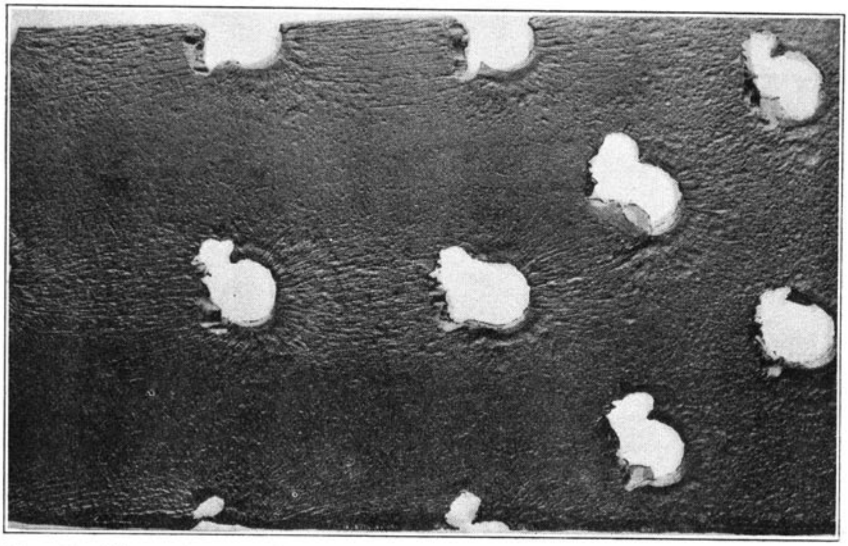

Fig. 12. Water Side of Crown Sheet Shown in Fig. 11 Showing Corrosion Following Lines of Stress

high stresses. It has not been the purpose of this investigation to suggest how boilers should be made or to find fault with those already in service. The only question in regard to boiler design or workmanship to be answered in this investigation was—were the embrittled boilers of the standard of design and workmanship expected at the time they were manufactured? In almost every case investigated the representative of an insurance company passed on the boiler as representing the average workmanship at the time the boiler was built. Furthermore these boilers all bore the A. S. M. E. and the insurance companies' stamps as being satisfactory when they left the manufacturer's plant. Naturally the boilers built in 1905 had punched holes, and in them drifting was common, and calking excessive. Newer boilers had holes drilled from the solid with the plates in position; butt seams replaced lap seams; calking became less in evidence and was practised both inside and outside. Seams laid up as perfectly as it was possible to do in a practical manner by the art of 1924 have been embrittled as well as old poorly fitting seams manufactured in 1905. If embrittlement were the result of poor workmanship it would appear evident that if the good boilers of 1924 had trouble, then certainly all the boilers of 1905 should have cracked. Furthermore, boilers with evidence of extremely poor workmanship have served for

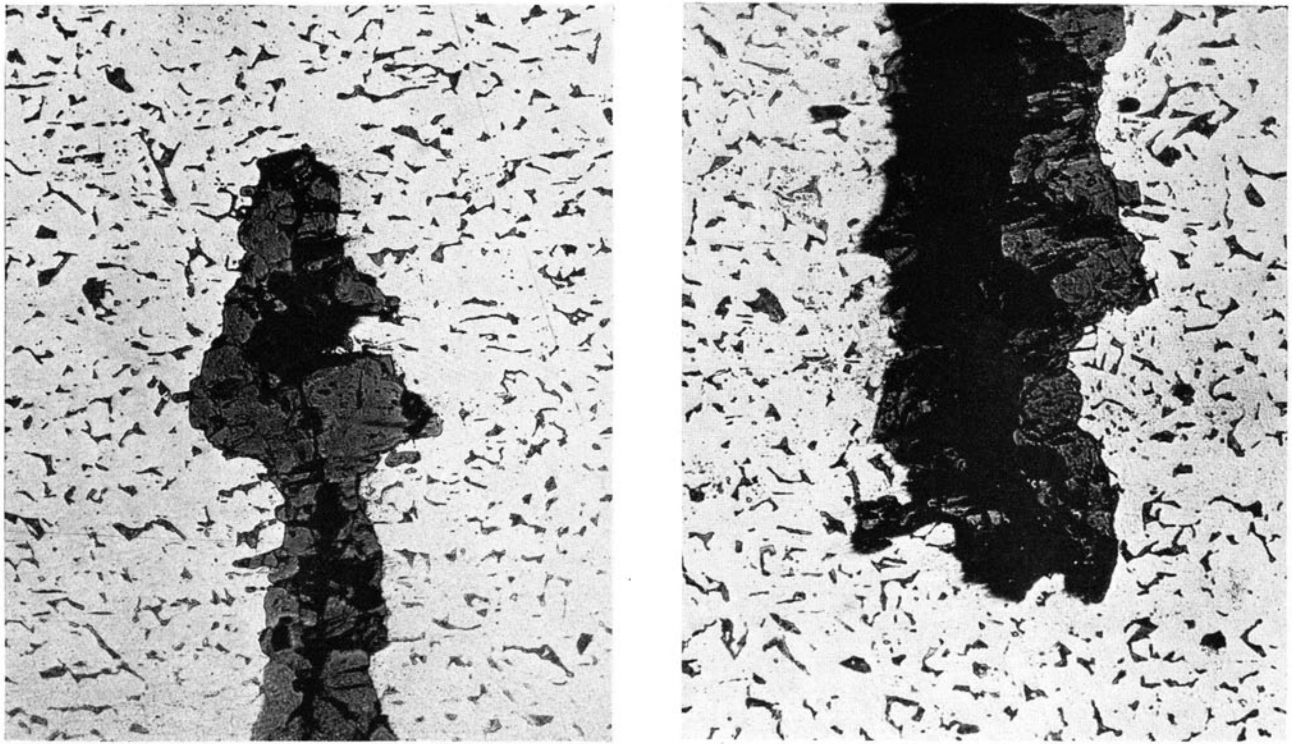

FIG. 13. MICROGRAPHS OF CORROSION CRACKS IN PLATE SHOWN IN FIGS. 11 AND 12
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thirty years without suffering from embrittlement, and when taken apart have been found free from trouble of this nature. All the evidence gained from a complete and unbiased examination of embrittled boilers points to the conclusion that poor workmanship alone never caused any boiler to become embrittled.

Operation

The condition of operation of a boiler may be a large contributing factor in causing trouble. The effects of high rating, hot gases in contact with the metal parts of the boiler, frequent hydrostatic tests, excessive calking of leaky seams, and the presence of high operating stresses at high temperatures over prolonged periods of time are all to be considered in trying to ascertain the causes of embrittlement. Due consideration has been given to every conceivable factor which might contribute to this difficulty, but throughout the numerous cases encountered no one factor of operation was common to all. A crack might be found in a seam where the colder feed water was on one side and the hot gases on the other; this would point toward high temperature differentials being a contributing factor; but the next crack might occur in the setting, with small temperature difference in the seams. Likewise, a boiler working at high rating might crack, while the next instance of cracking might be found in a boiler operating at low rating. Boilers designed for a pressure of 200 lb. per sq. in., with a factor of safety of 6, have cracked when operated at 150 lb.; and so forth. The files of the investigation contain numerous reports of instances of embrittlement which indicate that no one factor of operation or boiler design is common to the many cases of failure.

Feed Water

In the plans, specifications, and descriptions of new power plants given in the technical and trade journals little if any reference is made as to the source of water supply and the water treatment given. It is assumed that a steam boiler will use water and that water must be available. It has been the experience of those conducting this investigation that boiler operators knew less about the water supply than about any other part of the plant, and that only a very few could tell what type of water was being used.

On examining the mass of data collected from cases of embrittled boilers it could be clearly seen that the type of feed water used in embrittled boilers was apparently the only common factor. When the feed water used in such cases was analyzed the fact was disclosed that sodium carbonate was always present in considerable quantity while

the sulphate content was much lower. The boiler waters showed the presence of a high alkalinity with a correspondingly small sulphate content.

Hardness in boiler feed water can be considered roughly under two heads, carbonate hardness and sulphate hardness. In carbonate hardness the carbonates of magnesium or calcium are present in excess and only a small amount of the corresponding sulphates is found. This type of hardness has commonly been termed "temporary hardness," since it decreases on heating. The sulphates of calcium and magnesium are changed but little on heating, and hardness due to the presence of these sulphates has been termed "permanent hardness." In some natural waters in the United States sodium bicarbonate is present in appreciable amounts and almost invariably the sulphate content is relatively low. When the water is heated in the boiler the sodium bicarbonate breaks down to give the carbonate, which in turn decomposes to give sodium hydroxide and carbon dioxide.

$$H_2O + Na_2\,CO_3 \rightarrow 2Na\,OH + CO_2$$

Water + sodium carbonate $\rightarrow$ sodium hydroxide + carbon dioxide

The extent of the decomposition of the carbonate depends upon the temperature, or steam pressure, and the partial pressure of the carbon dioxide. In a boiler the steam carries away the carbon dioxide, favoring the formation of the hydrate. Boilers have been found where over 90 per cent of the sodium carbonate has been changed to the sodium hydroxide.

Sodium hydroxide is found in nearly all boiler water since soda ash is a common boiler compound; but the percentage occurring is not nearly so high as that found in embrittled boilers, and, furthermore, sulphates are generally present also in large amounts. Table 3 gives the analyses of boiler waters commonly encountered and shows the high sodium sulphate content generally occurring.

If calcium or magnesium sulphates are present, soda ash is added to form the less soluble carbonates and soluble sodium sulphate.

$$Na_2\,CO_3 + Ca\,SO_4 \rightarrow Na_2\,SO_4 + Ca\,CO_3$$

Sodium carbonate + calcium sulphate $\rightarrow$ sodium sulphate + calcium carbonate

The sodium sulphate is increased, so that the addition of an excessive amount of soda ash would be necessary to bring about an excess over the sulphate in normal permanent hardness. A water containing small amounts of sulphates, however, could readily be changed

TABLE 3

ANALYSES OF WATERS WITH HIGH SULPHATE CONTENT TAKEN FROM BOILERS WHICH WERE NOT EMBRITTLED

No.	Steam Pressure Carried	Sodium Hydroxide	Sodium Carbonate	Total Alkalinity as Sodium Carbonate	Sodium Sulphate	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$
		Grains per U. S. Gallon				
1	150 lb. per sq. in. gage	2	10	13	200	15.4
2	175 " " " " "	5.8	6.1	14.2	42.2	2.9
3	175 " " " " "	7.6	19.9	30.5	71.5	2.4
4	125 " " " " "	36.3	8.7	59.5	102.4	1.7

to one in which the soda ash is in excess by soda ash treatment, and such types have been found in use in embrittled boilers.

Thus sodium carbonate may be present in the feed water in excess of the sulphate as a result of either one of two causes. First, naturally in a well water having the sodium carbonate present, and second, as the result of water treatment. The addition of an excess of soda ash will produce such a water, or it may result from the use of the zeolite process of softening. In this process the softening is accomplished by means of either a mineral or an artificial zeolite. The bicarbonates of calcium and magnesium are converted to bicarbonate of soda, and the sulphates of calcium and magnesium to sodium sulphate, thus furnishing a water with zero hardness. The zeolite is rejuvenated by treating with sodium chloride solution. This system, when used on a water having a lower sulphate than carbonate hardness, will produce a water in which the carbonate of soda content will predominate over the sulphate content resembling the feed waters used in boilers that have suffered from embrittlement.

The districts in the United States where embrittlement has occurred in boilers using well waters containing sodium bicarbonate can readily be isolated. The map in Fig. 14 shows the location of these districts. Much effort has recently been directed toward treating these natural waters so as to overcome the effect of the excess of sodium bicarbonate, and cases of embrittlement with these waters are apparently decreasing in number. The increase in the use of water

FIG. 14. AREAS IN WHICH BOILERS USING WELL WATERS HAVE BEEN EMBRITTLED

treatment on surface waters low in sulphates has brought about an increase in the use of the soda ash and zeolite systems of softening. Naturally, waters having too high a sodium carbonate content as a result of either of these systems of water treatment cannot be isolated in any particular districts, since low sulphate surface waters occur in practically all sections of the country. As a result of this trend in water treatment the number of cases of embrittlement resulting from the use of these types of softened waters is increasing.

Table 4 gives the analyses of seven of the waters used in embrittled boilers, and shows the type of feed water common to every case of boiler embrittlement encountered. The first five are waters which have been zeolite treated, in the sixth case soda ash treatment has been used, and the last is a natural sodium carbonate water. The table also shows that none of these waters meets the A. S. M. E. recommendation as to sulphate—carbonate ratio. No embrittlement has ever been experienced with waters meeting this code recommendation.

Table 5 gives the analyses of seven waters taken from boilers in plants which have suffered from embrittlement and illustrates to what extent the hydroxide is formed.

TABLE 4

ANALYSES OF FEED WATERS USED IN EMBRITTLED BOILERS

No.	Source of Feed Water	Steam Pressure, lb. per sq. in.	Treatment Used	Calcium Carbonate	Magnesium Carbonate	Sodium Carbonate	Sodium Sulphate	Sodium Chloride	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$ Recommended by A. S. M. E.
				Grains per U. S. Gallon						
1	Lake....................	200	Zeolite	0.15	0.10	9.33	2.23	1.10	0.23	2.0
2	River....................	250	"	0.0	0.0	11.47	10.30	3.18	0.90	3.0
3	Lake....................	200	"	0.0	0.0	5.83	1.63	1.25	0.28	2.0
4	Well....................	30	"	0.0	0.0	18.9	2.0	1.6	0.10	1.0
5	Lake....................	225	"	0.20	0.29	8.90	1.50	1.50	0.17	2.0
6	Lake....................	265	Lime-Soda	0.41	0.41	4.00	2.10	1.34	0.52	3.0
7	Well....................	225	None	3.16	1.98	9.05	0.12	10.50	0.01	3.0

TABLE 5

ANALYSES OF BOILER WATERS TAKEN FROM EMBRITTLED BOILERS

No.	Source of Feed Water	Steam Pressure, lb. per sq. in.	Treatment Used	Sodium Hydroxide	Sodium Carbonate	Sodium Sulphate	Sodium Chloride	Total Alkalinity as Sodium Carbonate	Ratio Sodium Sulphate / Alkalinity as Sodium Carbonate	Ratio Sodium Sulphate / Alkalinity as Sodium Carbonate Recommended by A. S. M. E.
				Grains per U. S. Gallon						
1	Lake....................	200	Zeolite	85.4	69.2	44.7	27.3	188.0	0.24	2.0
2	River....................	250	"	24.3	10.5	36.2	24.4	44.5	0.81	3.0
3	Lake....................	200	"	216.0	74.9	56.6	87.5	361.0	0.15	2.0
4	Well....................	30	"	25.6	25.5	13.3	33.9	61.1	0.21	1.0
5	Lake....................	225	"	63.2	11.3	14.9	18.7	94.8	0.15	2.0
6	Lake....................	265	Lime-Soda	99.2	25.9	82.6	45.0	164.9	0.50	3.0
7	River....................	60	Zeolite	51.2	12.4	3.6	...	84.1	0.04	1.0

TABLE 6

ANALYSES OF BOILER WATERS TREATED TO INCREASE THE SULPHATE-CARBONATE RATIO

No.	Source of Feed Water	Treatment Used	Sodium Hydroxide	Sodium Carbonate	Sodium Sulphate	Total Alkalinity as Sodium Carbonate	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$ Recommended by A. S. M. E.
			Grains per U. S. Gallon					
1	Well	Lime and Acid	22.	9.	90.	38.	2.4	2.0
2	Lake	Zeolite and Acid	28.2	5.3	89.8	42.7	2.1	2.0
3	Lake	Zeolite and Acid	22.0	15.4	116.1	46.2	2.5	2.0
4	Lake	Zeolite and Acid	36.3	14.6	119.7	55.4	3.1	3.0
5	Well	Lime and Aluminum Sulphate	14.1	17.0	72.8	36.6	2.1	2.0

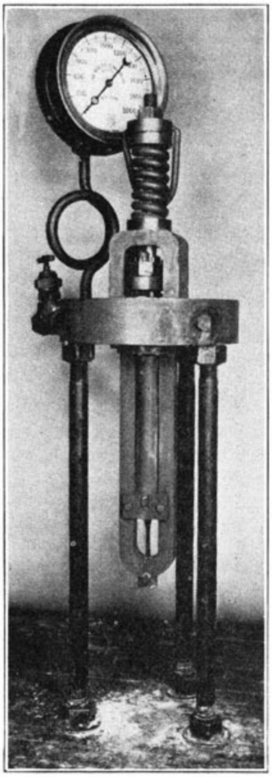


FIG. 15. TENSION SECTION OF APPARATUS USED IN EMBRITTLEMENT TESTS

Table 6 gives the analyses of waters taken from boilers which have been operated on zeolite-treated waters and natural sodium carbonate waters subsequently treated to meet the recommended sulphate-carbonate ratio. No embrittlement has ever been encountered in plants having waters such as these in the boilers.

IV. LABORATORY INVESTIGATION

11. *Reproduction of Embrittlement.*—The fact that embrittlement cracks were apparently intercrystalline suggested a means of attacking the problem in the laboratory. Except in cases of embrittlement the occurrence of intercrystalline cracking in boiler plate had never been reported under conditions which simulated boiler operation. A few isolated instances where selective corrosion had attacked the grain

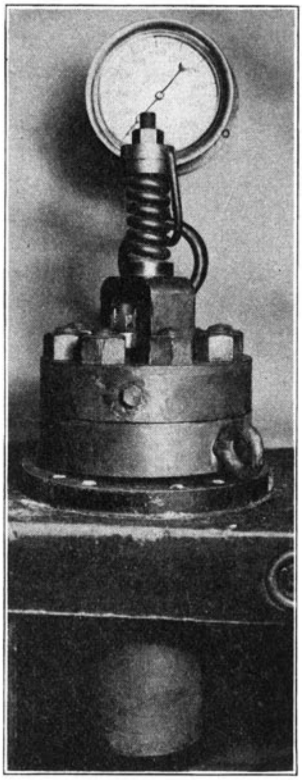


FIG. 16. TEST CONTAINERS USED IN EMBRITTLEMENT TESTS

boundaries of steel had been noted but the conditions under which this occurred were such as could not be encountered in operation. Cracks in boiler plate subjected to high stresses, impact tests, fatigue tests, corrosion-fatigue, etc., are almost invariably transcrystalline and follow the line of maximum stress. They may pass along one or two grain boundaries, but in general are transcrystalline.

The cracks in embrittled boiler plates are in general found to be intercrystalline and it is the exception when they cut across a grain. This observed peculiarity has been used as a means of detecting embrittlement cracks. Since this distinct difference could be found between cracks due to normal failure and those resulting from embrittlement, attempts were made early in the investigation to reproduce this type of cracking at will under known test conditions. These at-

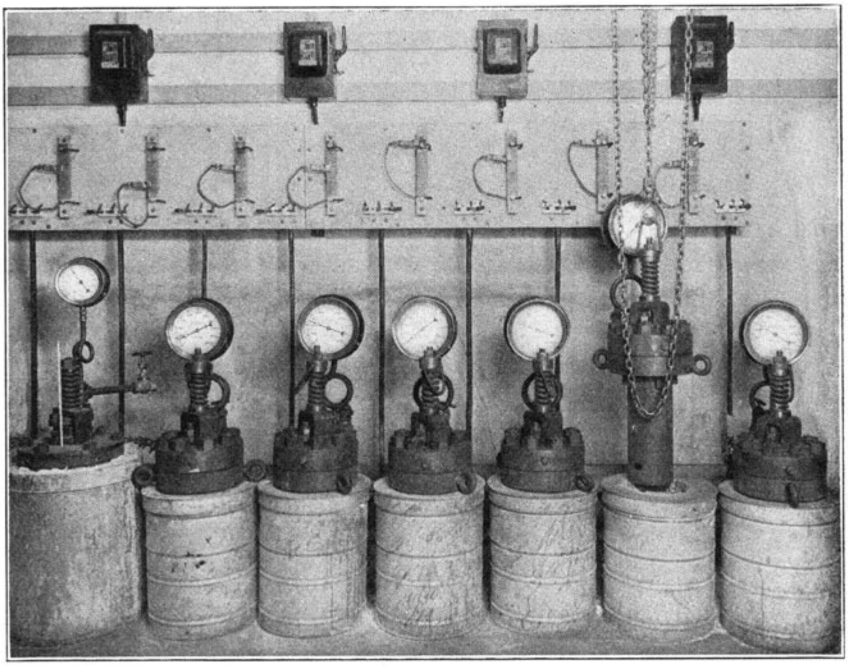


FIG. 17. TEST UNITS USED FOR HIGHER PRESSURE TESTS

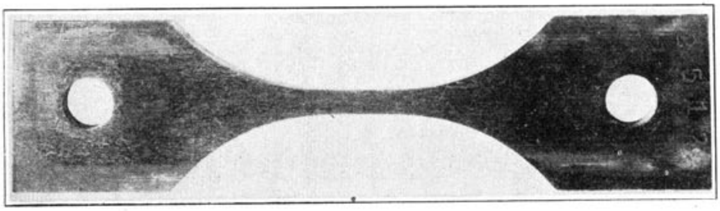
tempts met with success, and thus a means was immediately placed at the disposal of the investigation of studying the conditions under which embrittlement occurred and methods of preventing its occurrence.

An account of the earlier work done on the reproduction of embrittlement in boiler plate is given in Engineering Experiment Station Bulletin No. 155. The conclusions drawn from the laboratory tests reported in that bulletin were as follows:

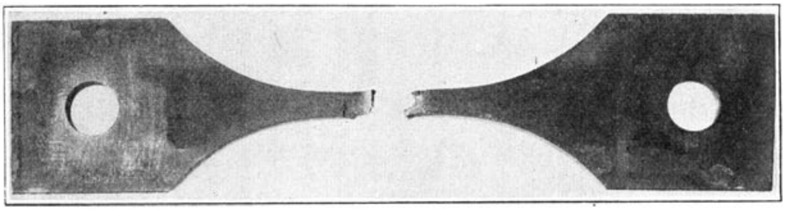
(1) Two conditions must be present simultaneously to cause embrittlement of mild steel in the test containers; first, the actual stress must be above the region of the yield point of the metal; and second, the concentration of sodium hydroxide must be in excess of 350 grams per liter (about 20 000 grains per gallon).

(2) Solutions of salts occurring in boiler water other than sodium hydroxide did not affect the stressed metal.

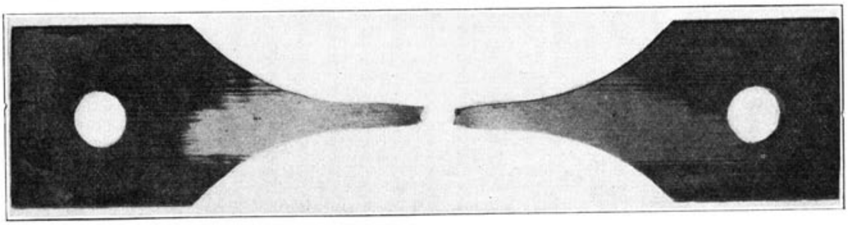
(3) Pure iron cracked as well as regular boiler plate and the introduction of nickel up to 3.5 per cent as a constituent of the steel did not prevent the cracking.



Test Specimen



Fracture of Embrittled Specimen



Fracture of Unembrittled Specimen

FIG. 18. TEST SPECIMENS

TABLE 7

CHEMICAL ANALYSES OF STEELS TESTED

Reference	Description of Material	Carbon per cent	Manganese per cent	Phosphorus per cent	Sulphur per cent	Silicon per cent	Nickel per cent
F.S.	Flange Steel	0.18	0.45	0.012	0.027	....	....
M.I.	Magnetic Iron	0.023	0.017	0.003	0.010	0.01	....
Ni	Nickel Steel	0.18	0.54	0.035	0.028	0.23	2.62
Si	Silicon Steel	0.34	0.75	0.027	0.034	0.29	....
Mn	Low Manganese Steel	0.35	2.13	0.020	0.026	0.023	....
Acid	Acid Open Hearth Steel	0.42	0.46	0.036	0.044	0.051	....
W.	Steel from Embrittled Boiler	0.22	0.55	0.015	0.035	....	....
G.	Old German Steel Plate	0.06	0.33	0.012	0.035	....	....
Izett	Special German Steel Plate	0.17	0.41	0.020	0.031	0.053	0.030
E.	English Steel	0.16	0.35	0.018	0.018	0.040	....
1020	S.A.E. No. 1020 Steel	0.18	0.56	0.012	0.040	0.005	....
1112	S.A.E. No. 1112 Steel	0.15	0.65	0.086	0.156	0.028	....

TABLE 8

TENSION TESTS OF STEELS TESTED

Reference	Description of Material	Heat Treatment	Yield Point	Ultimate Tensile Strength	Reduction of Area
			lb. per sq. in.		per cent
F.S.	Flange Steel	As received	35 200	60 400	61.
Sorbitic	Flange Steel	Oil quenched 850° C. Reheated to 600° C.	53 000	68 600	64.7
Spheroidized	Flange Steel	Oil quenched 850° C. Reheated to 675° C. 8 hours.	50 600	61 100	67.0
M.I.	Magnetic Iron	Annealed at 950° C.	30 000	50 700	72.0
Ni	Nickel Steel	As received	45 000	75 300	59.3
Si	Silicon Steel	As received	43 000	87 000	48.0
Mn	Low Manganese Steel	As received	47 000	103 000	55.0
Acid	Acid Open Hearth Steel	As received	33 000	74 000	46.0
W.	Steel from Embrittled Boiler	As received	33 400	65 400	50.0
G.	Old German Steel Plate	As received	32 000	56 500	65.3
Izett	Special German Steel Plate	As received	32 000	56 500	67.5
E.	English Steel	Annealed at 950° C.	27 000	50 000	....
1020	S.A.E. No. 1020 Steel	Annealed at 950° C.	31 000	56 000	67.5
1112	S.A.E. No. 1112 Steel	Annealed at 950° C.	41 000	63 500	58.0

(4) Cold work did not make the steel more susceptible to embrittlement.

12. *Testing Apparatus.*—The apparatus used for the reproduction of embrittlement at higher pressure is shown in Figs. 15, 16, and 17. The idea of a constant spring load is used. The containers were furnished through the courtesy of the Babcock & Wilcox Co., and are capable of holding steam pressures up to 2000 lb. Figure 18 shows the regular test specimen before test, one broken in a regular tension test, and one broken in the embrittling apparatus.

13. *Materials Embrittled.*—Table 7 gives the chemical analyses and Table 8 the physical properties of the metals tested.

14. *Procedure in Tests.*—The specimen to be tested was measured with a micrometer and the area calculated. The load necessary to give the required stress was calculated and the compression of the standardized spring to give this load determined. The specimen was then pinned in position and the spring tightened. When the spring had been compressed to the right length the gland was tightened and the upper part of the apparatus placed on the container in which the desired solution had been previously placed. After the parts had been tightly bolted together the apparatus was placed in an electric furnace and heated until the desired pressure was obtained. A record of the pressure, temperature, and spring length was taken at regular intervals. When embrittlement had progressed sufficiently to break the specimen the spring forced the plunger up, thus indicating that the specimen had broken.

The average area of the test specimens was 0.05 sq. in. The accuracy of the estimated load on the specimen was within 1000 lb. per sq. in. when the stress was in the neighborhood of 40 000 lb. per sq. in. In calculating the stress, allowance was made for the stress added by the steam pressure acting on the plunger.

V. Test Data on Embrittlement

15. *Tests Conducted.*—Several series of tests were conducted in the attempt to answer the following questions in regard to the embrittling action:

(1) Can a time factor be established which will serve to indicate the possibility of cracking at lower concentration of sodium hydroxide over prolonged periods?

(2) Is the rate of cracking dependent on the stress? Is it possible to predict whether cracking will take place over a long period of time at a stress below the yield point?

TABLE 9

EFFECT OF CONCENTRATION OF SOLUTION ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 100 and 500 lb. per sq. in.
Tension on Specimen, 54 000 lb. per sq. in.

Steam Pressure lb. per sq. in.	Concentration Sodium Hydroxide Solution grams per liter	Time of Cracking days
100	425	3
100	380	4
100	350	5½
100	310	9
100	200	30
500	330	1¼
500	280	½
500	240	¾
500	200	1½
500	150	4½
500	125	14½

(3) What is the effect of changing the chemical composition of the steel?

(4) Can a retarding influence be produced by heat treatment of the boiler plate?

(5) What influence does increased steam pressure have upon the rate of cracking?

(6) What is the effect of increasing the sodium chloride content?

The tests that were conducted with the object of obtaining information to answer these questions were run with special precautions to guard against results which might not be representative. The total number of specimens tested was about 300. Duplicate tests were made whenever definite conclusions were to be drawn from the results. Specimens which did not fail with the solutions and stresses employed in the original test were later cracked with standard solutions and stresses, showing that they were not resistant to the general attack.

16. *Data from Tests.*—The results of the tests on the various metals tested are given in Tables 9 to 15 inclusive. These indicate the following:

(1) With reference to the relation of time of cracking to concentration of solution, the data given in Table 9 and shown in graph form in Fig. 19 indicate that the time of cracking varies inversely with the concentration, and show that cracking can be predicted at a much lower concentration than heretofore found. It would not be unreasonable to predict cracking at a concentration as low as 70

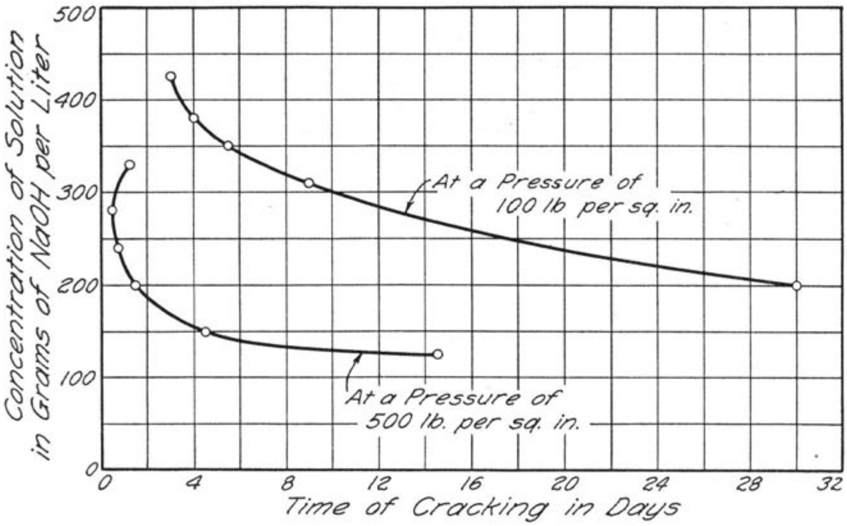


FIG. 19. RELATION OF TIME OF CRACKING TO CONCENTRATION

grams per liter, or approximately 4000 grains per gallon under the test conditions. This concentration is only 15 times that reached in the main body of many boilers.

(2) As to the effect of total stress on the rate of cracking, if it is assumed that the final rupture is purely a static failure produced when the intercrystalline cracking has weakened the metal until the stress produced by the spring and the steam action is sufficient to cause failure, then the rate of penetration of the intercrystalline cracking can be calculated.

In order to determine this rate the following calculations were used:

$$T = \frac{a - \frac{L}{U}}{t}$$

where T = time rate of penetration in sq. in. per hr.
a = area of specimen in sq. in.
L = total load on plunger in lb. (spring plus steam)
U = ultimate tensile strength of specimen in lb. per sq. in.
t = time of cracking in hr.

The results of tests run at a pressure of 500 lb. per sq. in. and at the optimum concentration, 300 grams per liter, with varying inten-

TABLE 10

EFFECT OF TOTAL STRESS ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.

Concentration of Solution, 300 grams Sodium Hydroxide per liter

Total Load lb. per sq. in.	Time of Cracking hr.	Time Rate of Penetration sq. in. per hr.
54 000	12	0.0004
54 000	12	0.0004
44 000	24	0.0005
35 500	36	0.0005
33 000	No crack in 35 days	0.0000

sities of stress, are tabulated in Table 10. These results indicate that for the steel tested the time rate of penetration is independent of the total stress once the stress passes the region of the yield point. Below the yield point no cracking occurs. This shows that apparently for static loads no cracking can be predicted even over prolonged periods of time when the localized stress is below the region of the yield point of the boiler plate.

(3) In order to investigate the effect of the composition of the steel, specimens of all the steel listed in Tables 7 and 8 were tested, and their corresponding time rate of cracking determined. The results as given in Table 11 show that all the steels cracked within a reasonable time. The acid, the old German, the silicon, and the mild manganese steel cracked at an appreciably faster rate than normal boiler plate. The other steels, including some from embrittled boilers, all cracked at about the same rate. Particular attention should be paid to steel No. 1112, a high phosphorus and sulphur steel, which had a time rate much lower than those of pure iron and boiler plate. This indicates that even the high phosphorus and sulphur content does not make the steel more susceptible to cracking of this nature.

The English steel tested was furnished through the courtesy of Dr. Walter Rosenhain, who has done considerable work on the intercrystalline cracking of metals. He conducted a series of tests on this steel "with a view of producing fracture under prolonged loading in mild steel stressed to various intensities at a temperature of 300° C. in air" and showed that this treatment failed to produce fracture even after five years of exposure. In commenting on this he said, "This certainly suggests that some subsidiary agency of a corrosive nature is necessary to produce failure in a reasonable time, although it is quite possible that the particular sample of steel which I employed

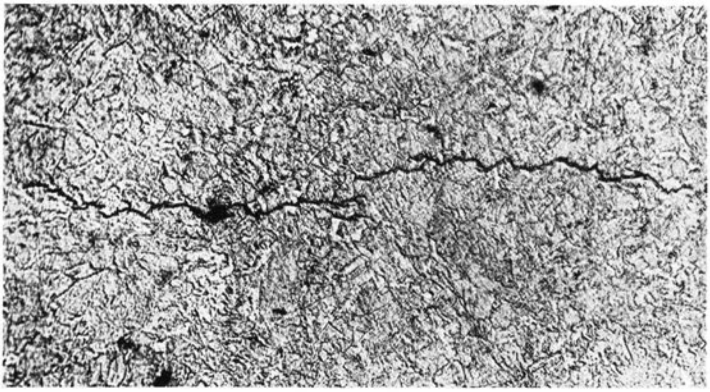
TABLE 11

EFFECT OF CHEMICAL COMPOSITION OF STEEL ON TIME RATE OF EMBRITTLEMENT

Steam Pressure, 500 lb. per sq. in.

Concentration of Solution, 300 grams Sodium Hydroxide per liter

Reference	Description of Material	Yield Point	Ultimate Tensile Strength	Total Load During Test	Time of Cracking hr.	Time Rate of Penetration sq. in. per hr.
		lb. per sq. in.				
F.S.	Flange Steel	35 200	60 400	54 000	12	0.0004
F.S.	Flange Steel	35 200	60 400	35 500	36	0.0005
M.I.	Magnetic Iron	30 000	50 700	45 000	7	0.0005
Ni	Nickel Steel	45 000	75 300	57 000	22	0.0005
Si	Silicon Steel	43 000	87 000	60 000	8	0.0018
Acid	Acid Open Hearth Steel	33 000	74 000	54 000	12	0.0010
Mn	Low Manganese Steel	47 000	103 000	64 000	22	0.0008
W.	Steel from Embrittled Boiler	33 400	65 400	54 000	24	0.0004
G.	Old German Steel Plate	32 000	56 500	40 000	13	0.0010
Izett	Special German Steel Plate	32 000	56 500	40 000	24	0.0004
Izett	Special German Steel Plate	32 000	56 500	40 000	20	0.0005
E.	English Steel	Specimen too small for regular tests—Cracked in caustic				
1020	S.A.E. No. 1020 Steel	31 000	56 000	49 000	10	0.0004
1112	S.A.E. No. 1112 Steel	41 000	63 500	54 000	54	0.0001
1112	S.A.E. No. 1112 Steel	41 000	63 500	54 000	60	0.0001



Sorbitic Steel

Spheroidized Steel

FIG. 20. MICROGRAPHS OF EMBRITTLED SPECIMENS OF HEAT-TREATED STEEL
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TABLE 12

EFFECT OF HEAT TREATMENT ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.

Concentration of Solution, 300 grams Sodium Hydroxide per liter

Steel Tested	Yield Point	Ultimate Tensile Strength	Total Load During Test	Time of Cracking	Time Rate of Penetration
	lb. per sq. in.			hr.	sq. in. per hr.
Untreated..................	35 200	60 400	54 000	12	0.0004
Spheroidized................	50 600	61 100	54 000	12	0.0004
Sorbitic....................	53 000	68 600	59 000	14	0.0005
Sorbitic....................	53 000	68 600	49 000	28	0.0005
Sorbitic....................	53 000	68 600	38 000	No crack in 20 days	0.0000

was not one subject to intercrystalline fracture under prolonged loading." This steel when tested at a load above its yield point cracked in a period of less than three days. Due to the specimens being so small no quantitative data are available as to time rate of penetration. The test does serve to illustrate, however, that while this metal would normally stand a load of high magnitude for years without failure the presence of the caustic solution brought about fracture very rapidly.

Fry* recently reported a new type of steel manufactured by Krupp in Germany which retained high impact values even after being cold worked. He also reported the results of bending specimens of this steel and subjecting them to strong caustic attack, stating that the caustic did not embrittle the steel. Three different samples of this steel called Izett were obtained and under test showed no better resistance to embrittling attack than the regular American boiler plate.

(4) As to the effect of heat treatment, the suggestion† has been made that a heat treatment which will make the grain boundaries very rough or indistinct, such as exists in the sorbitic and spheroidized condition, might have a retarding influence on the crackings.

Tests were accordingly run on samples of flange steel previously heat treated so as to produce these types of structure. The results as tabulated in Table 12 show that the existence of the sorbitic or spheroid condition does not stop the cracking of the boiler plate. Micrographs are shown in Fig. 20. A point of particular interest is

*Krupsche Monatschefte, Vol. 7, 1926, pp. 185-196.

†Rosenhain, W., Iron and Steel Institute, 1927. Engineering, Sept. 23, 1927.

TABLE 13

EFFECT OF STEAM PRESSURE ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Concentration of Solution, 200 grams Sodium Hydroxide per liter

Steam Pressure lb. per sq. in., gage	Time of Cracking hr.	Time Rate of Penetration sq. in. per hr.
100	720	0.000013
500	30	0.00017
1000	10	0.0013

that making the steel sorbitic raises the yield point; but the cracking takes place below this new yield point, yet above the yield point of the untreated metal. This shows that cracking is not a real function of the yield point but happens to require an initial stress which is in the region of the yield point. The results obtained from testing a cold-rolled specimen previously reported* showed that raising the yield point by cold work also raised the stress necessary for embrittlement, but not in proportion to the rise in yield point produced by cold work.

(5) As to the effect of higher steam pressures on the rate of cracking, the results of tests conducted at various steam pressures are tabulated in Table 13, and show that the time of cracking decreases with an increase in temperature. These results also illustrate the fact that the concentration of solution required for the optimum cracking time would decrease with an increase in pressure. If the highly concentrated solutions necessary for the lower pressures are used at the higher pressures the solutions attack the steel with the free evolution of hydrogen and corrode the specimen instead of cracking it.

(6) In studying the effect of adding sodium chloride, tests were conducted with varying amounts of sodium chloride at a pressure of 500 lb. per sq. in., and 300 grams of sodium hydroxide per liter gave the results shown in Table 14. These show that for this concentration small amounts of sodium chloride accelerate the cracking, while larger amounts tend to reduce this effect. When 150 grains of sodium chloride were added per liter a rapid generation of pressure occurred as soon as a pressure of 500 lb. per sq. in. was reached. The removal of the source of heat caused this pressure to decrease as rapidly and when heat was reapplied it returned. This phenomenon occurred also with a

*See "The Cause and Prevention of Embrittlement of Boiler Plate," Univ. of Ill. Eng. Exp. Sta. Bul. 155, 1926.

TABLE 14

EFFECT OF INCREASING SODIUM CHLORIDE CONTENT ON TIME RATE OF EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.

Concentration of Solution, 300 grams Sodium Hydroxide per liter

Sodium Chloride Content grams per liter	Time of Cracking hr.
0	24
15	18
30	7
50	10
100	15
150	Gas generated stopped test

pure sodium chloride solution without the caustic. No residual gas remained on cooling. This fact eliminated the possibility of hydrogen being generated and suggested that hydrochloric acid was being formed. The vapor pressure of hydrochloric acid from the sodium chloride ionized in the water at a temperature corresponding to a steam pressure of about 500 lb. per sq. in. must become greater than 500 lb. and consequently it increases the pressure. On cooling the hydrochloric acid recombines with the sodium hydroxide.

VI. INHIBITION OF EMBRITTLEMENT

17. *Data from Power Plants.*—When the attention of the earlier investigators was first called to the fact that sodium hydroxide might be a contributing factor in the embrittling of boilers, attempts were made to stop the formation of the hydroxide in the boiler. The addition of organic matter was tried with no marked success, since it did not retard the decomposition of the carbonate to any extent. Early in 1914 attempts were made at the University of Illinois power plant to lower the sodium carbonate content in the feed water by adding magnesium sulphate. This formed sodium sulphate and decreased the sodium carbonate content. Later this treatment was changed to one by sulphuric acid. The regular lime treatment was applied and then sufficient sulphuric acid added to neutralize about two-thirds of the sodium carbonate in the water. Before adopting this system of treatment difficulty had been experienced with all the boilers in the plant and since its adoption no further difficulty of this nature has been

TABLE 15

ANALYSES OF WATER FROM EVAPORATORS USING SODIUM CARBONATE WATER SUPPLY

No.	Calcium Carbonate	Magnesium Carbonate	Sodium Carbonate	Sodium Sulphate	Sodium Chloride	Iron and Aluminum Oxide	Silica
	Grains per U. S. Gallon						
1	0.21	0.00	0.70	0.54	0.34	0.00	0.12
2	trace	trace	0.92	0.78	0.68	trace	0.25

encountered. A recent thorough examination of these boilers, involving removing of rivets, and a thorough examination of rivet holes, showed that after ten years operation on water treated by this system the boilers were free from any indications of embrittlement. Within recent years the practice of keeping a definite amount of sodium sulphate in all boilers using sodium carbonate waters has become popular with large power plant operators so that at present over twenty plants are using this means to inhibit embrittlement. The increase of sulphate is accomplished by various means, some plants using acid, while others use aluminum sulphate, iron sulphate, etc. Some plants which had trouble with embrittlement have changed the sources of supply of the boiler feed water to ones free from sodium carbonate, with the elimination of the difficulty.

A local power plant operating on the same type of feed water supply as that used at the University of Illinois recently encountered serious difficulty in the form of embrittled drums. This power plant operated the boilers at about the same pressure as the University boilers and with the same makeup. The only apparent difference was that the University feed water was treated to increase the sulphate while the other plant's supply was not. After eight years of use these boilers were badly embrittled while the University boilers operating on the sulphate-treated water are still free from embrittlement.

The use of sulphate treatment is very limited, and since the occurrence of embrittlement is apparently on the increase, other methods of stopping it have been diligently sought. The use of a satisfactory sulphate ratio on waters low in calcium and magnesium is possible, but when these salts are present it becomes practically impossible to keep the recommended ratios at the higher pressures. Furthermore, the use of sulphuric acid is only to be recommended when the direct supervision of a man conversant with the use of chemicals is

TABLE 16

EFFECT OF SODIUM SULPHATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.

Stress on Specimen, 50 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Time of Cracking days	Ratio $\frac{\text{Sodium Sulphate}}{\text{Sodium Hydroxide}}$	Ratio $\frac{\text{Sodium Sulphate}}{\text{Alkalinity as Sodium Carbonate}}$
135	1½	0.0	0.0
120	1¾	1.6	1.1
127	3	2.1	1.5
120	3	2.6	1.8
140	2	3.1	2.2
120	4	4.0	2.8
135	No crack in 30 days	5.0	3.6

available. An overdose of this medicine may result in more trouble than the original disease, and consequently operators and men responsible for large power units hesitate to use acid under average conditions of operation.

When evaporators are used on alkaline water it becomes difficult to get a water free from sodium carbonate. Table 15 gives the analyses of evaporated water from a few such waters. The acid treatment of these waters is almost impossible. The addition of sodium sulphate defeats the purpose of evaporation; consequently, a new inhibitant is sought for this type of water.

The inhibitant must be non-corrosive, must stop embrittlement in relatively small amounts, over-treatment must cause no trouble, the treatment must require but a small amount of chemical control, and be inexpensive. Work has been conducted with good success toward the finding of inhibitants to meet these conditions.

18. *Data from Laboratory.*—The results of the work conducted on the use of sodium sulphate as an inhibiting agent was published in Bulletin No. 155. This showed that for pressures up to 100 lb. per sq. in. the embrittlement could be stopped entirely by maintaining a ratio of sodium sulphate to sodium carbonate alkalinity of 1 to 1 in the boiler. In the laboratory tests a ratio of 2 parts of sodium sulphate to one part of sodium hydroxide was necessary but when it is considered that in boilers operating at 100 lb. hardly 50 per cent of the carbonate goes to hydroxide a ratio of 1 to 1 is seen to be amply safe.

TABLE 17

EFFECT OF PHOSPHATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount PO_4 radical in Solution grams per liter	Time of Cracking hr.	Ratio $\frac{PO_4}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{PO_4}{\text{Alkalinity as Sodium Hydroxide}}$
295	0	24	0.0	0.0
280	0.4	20	0.0010	0.0014
280	0.6	No crack in 13 days	0.0015	0.0021
280	0.6	No crack in 30 days	0.0015	0.0021
280	1.0	No crack in 13 days	0.0025	0.0035
280	1.0	No crack in 17 days	0.0025	0.0035
280	2.0	No crack in 13 days	0.0050	0.0070

The results of tests conducted at 500 lb. per sq. in. pressure are given in Table 16. In the tests previously reported it was shown that to produce the inhibiting effect of sodium sulphate the solution must be brought around the specimen in such a manner that any salt precipitating out will form on the test specimen. To do this the specimen was surrounded by steel allowing but $\frac{1}{32}$ in. of space between the specimen and the surrounding steel. A dilute solution of the salts was originally used and this was slowly concentrated by the removal of steam. When the proper caustic concentration was reached the test was started.

To adapt this to the higher pressures, tests were conducted using the lowest concentration of caustic that would produce cracking in a reasonable length of time. This was done so that if the inhibiting action is due to a solubility effect, the lower the sodium hydroxide content the higher will be the solubility of the sulphate. In this manner the most protective ratio can be obtained. If sodium chloride is also introduced then the best conditions for cracking are obtained and if the sulphate can stop embrittlement under this ideal condition, the conclusion can be drawn that the ratios obtained are protective. The results show that a ratio of $Na_2\ SO_4$ to $Na\ OH$ of 5.0 to 1 or of $Na_2\ SO_4$ to alkalinity as $Na_2\ CO_3$ of 3.5 to 1 stops embrittlement at a

TABLE 18

EFFECT OF TANNIC ACID IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in.

Concentration of Sodium Hydroxide Solution grams per liter	Amount Tannic Acid Added to Solution grams per liter	Time of Cracking hr.	Ratio $\frac{\text{Tannate}}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{\text{Tannate}}{\text{Alkalinity as Sodium Hydroxide}}$
250	0	20	0.0	0.0
275	5	20	0.013	0.018
290	10	No crack in 30 days	0.024	0.034
290	10	No crack in 20 days	0.024	0.034
275	15	No crack in 30 days	0.090	0.120
270	50	No crack in 10 days	0.130	0.185

pressure of 500 lb. per sq. in. This substantiates the correctness of the ratios suggested by the A. S. M. E. code.

The question of the inhibiting effect of the sulphate would seem to be that of solubility in the hydroxide. At lower pressures where higher concentrations of hydroxide are essential the solubility of the sulphate is lower, and less is required to inhibit the cracking. At higher pressures, with lower concentrations of hydroxide and higher temperatures, the solubility of the sulphate is higher, thus requiring more to be present before precipitation takes place.

The solubility effect, however, may not be the dominating factor, and electrolytic potential may have equal or greater importance. This may be due in the case of sulphate to the presence of a saturated solution in contact with the metal surface. In event of the electrolytic potential being a controlling factor in inhibiting embrittlement the use of salts of chromates, phosphates, tannates, acetates, etc., ought to be effective.

Laboratory tests show that these salts are very effective in stopping embrittlement. The results of the tests are given in Tables 17 to 19 inclusive.

The results of the tests on phosphate are given in Table 17. They indicate that comparatively small amounts of this radical will retard the embrittling action of sodium hydroxide. Thus as low as 0.6 grams

TABLE 19

EFFECT OF SODIUM ACETATE IN INHIBITING EMBRITTLEMENT OF FLANGE STEEL

Steam Pressure, 500 lb. per sq. in.
Stress on Specimen, 45 000 lb. per sq. in

Concentration of Sodium Hydroxide Solution grams per liter	Amount Sodium Acetate in Solution grams per liter	Time of Cracking hr.	Ratio $\frac{\text{Sodium Acetate}}{\text{Alkalinity as Sodium Carbonate}}$	Ratio $\frac{\text{Sodium Acetate}}{\text{Alkalinity as Sodium Hydroxide}}$
280	0	20	0.0	0.0
290	20	28	0.095	0.069
285	50	42	0.244	0.175
285	75	No crack in 25 days	0.37	0.263
290	100	No crack in 20 days	0.476	0.345

per liter of phosphate radical (PO_4) prevented embrittlement in the presence of 280 grams per liter of sodium hydroxide, at a steam pressure of 500 lb. per sq. in. The phosphate radical appears to be about 1500 times as effective as the sulphate.

The results of the tests in tannate are given in Table 18 and show that tannate if present with sodium hydroxide will stop the embrittling action.

Sodium acetate also proved to be helpful in retarding embrittlement as shown by the results tabulated in Table 19.

VII. DISCUSSION OF RESULTS

19. *Causes of Embrittlement in Steam Boilers.*—The results that have been obtained from the investigation of actual cases of embrittled boilers and experimental work in the laboratory can be briefly summarized as follows:

(1) In the cases of embrittlement investigated neither the design nor the workmanship of the boilers was responsible for the trouble.

(2) No fault could be found with the material of the boiler plate, the quality of which was fully up to specification requirements.

(3) Apart from the nature of the feed water used the operation of the boilers was satisfactory.

(4) An alkaline condition of the boiler water, with a low sulphate content, was found in all cases of embrittled boilers.

(5) The only material found in these boiler waters which has

been shown to have the effect of embrittling stressed steel is sodium hydroxide. The concentration of sodium hydroxide necessary to produce embrittlement is higher than that found in the main body of the boilers.

(6) Increasing the sulphate content has been found to be effective in stopping or inhibiting embrittlement, both in laboratory experiments and in operating steam plants.

(7) As a result of the experimental work new embrittlement inhibiting agents have been developed.

All the data obtained from steam plants show that boilers crack in an intercrystalline manner only when operated on alkaline waters low in sulphates. This cracking has been stopped by increasing the sulphate or lowering the sodium hydroxide content. Plants free from it for years have suddenly encountered trouble when an alkaline water has been used. The laboratory results show that sodium hydroxide is the only chemical in the water which would cause this kind of cracking on stressed steel. A correlation of these observed facts shows conclusively that the offending agent has been the sodium hydroxide in the boiler. The only questions which arise are—how does the caustic act in the seams? and how does a stress exist of a magnitude sufficient to cause the caustic attack to start? It can be shown that boilers with a factor of safety of around 5 have a calculated theoretical stress of 11 000 to 12 000 lb. per sq. in. between the rivet holes. In this calculation it is assumed that the rivet holes are theoretically in line, that stresses are evenly applied, and that all the metal is perfectly homogeneous and has exactly the same physical properties. Allowing for the concentration of stress at the edge of a rivet hole due to the discontinuity of the metal, the actual stress in the plate at a rivet hole becomes nearly three times the average stress in the plate or about 33 000 lb. per sq. in., approximately equal to the yield point strength of the boiler plate. When there is added to this the concentration of stresses brought about by the fact that practically the holes cannot be absolutely in line, that the riveting pressure causes slight deformation, that calking causes excess stresses, etc., there can be little doubt that a local stress of a magnitude about equal to that of the yield point strength exists. The tests conducted in the regular laboratory experiments represented steel under direct tension.

In the riveting of plates the rivet exerts an appreciable stress upon the metal immediately adjacent to the rivet hole due to the expansion of the rivet in the hole. Baumann* concludes that "even

*Baumann, Forschungsarbeiten Verein Deutscher Ingenieurewessens, Heft 252, 1922.

when riveting pressures barely sufficient to obtain properly formed and calkable rivet heads are used, the material in the plates is still stressed beyond its yield point." To verify this, samples of steel with small rivets forced into holes in the steel were put in caustic solution under steam pressure. When these were removed after three days small cracks were found radiating from the edges of the holes. The only stress in the steel was that produced by the action of the rivet filling the hole.

In some boilers a factor of safety as low as $3\frac{1}{2}$ has been used, yet the high resulting stresses alone have not produced embrittlement. The factors of safety used have resulted from years of experience in boiler design and operation, and use of boiler plate. Many examples of evidence of stresses of a magnitude equal to the yield point strength of boiler plate in boilers are available.

The laboratory results show that the presence of a concentration of about 4000 grains per gallon of sodium hydroxide will cause embrittlement of a piece of stressed steel. It has also been demonstrated that if the solution be allowed to penetrate between two plates as a thin film the time required to produce embrittlement cracking and likewise the concentration necessary are reduced. The fact that cracking occurs in a shorter period of time when the solution penetrates between two plates is capable of two explanations.

The first explanation is that, due to lack of circulation and reaction with the steel, the concentration increases locally. Analyses made of the coating on the iron after contact with the sodium hydroxide show it to be Fe_3O_4. The reaction to produce this is undoubtedly $3\ Fe + Na\ OH + 4H_2O = Fe_3\ O_4 + Na\ OH + 4\ H_2$. The Na OH merely acts as an accelerating agent by increasing the electromotive force of the solution with respect to the steel. The only materials actually entering into the reaction are iron and water. As the water is used it concentrates the caustic in the thin film of solution and increases the reaction.

The second explanation is that a thin film of liquid in immediate contact with two plates may have a higher activity than a large amount of solution surrounding a piece of steel. No statement can be made relative to the actual concentration in the seam. Baumann* has shown that concentration can take place in a theoretically constructed seam in which there was a possibility of diffusion but not outside leak. If the diffusion possibility were reduced so as to simulate actual boiler operation no doubt exists as to the possibility of ob-

*"Zur Sicherheit des Dampfkesselbetriebes," Berlin, 1927, pp. 109-116.

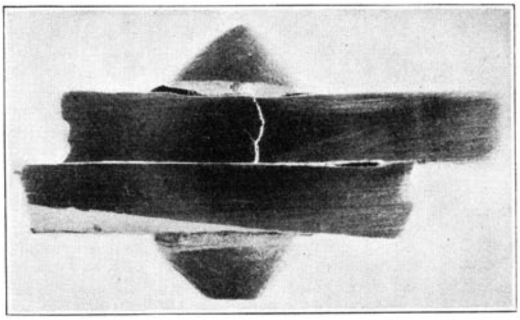

FIG. 21. SECTIONS OF EMBRITTLED SEAM SHOWING POINTS OF POSSIBLE CONCENTRATION

taining much higher concentrations than those obtained by Baumann. Berl* has reported the results of research on the possibility of concentration in seams and the effect of caustic soda solutions on iron at high pressures. He found that sodium hydroxide solutions of about 200 grams per liter readily attacked iron with the evolution of hydrogen at pressures around 100 atmospheres. He reported but little effect on steel of solutions of caustic of the concentration normally encountered in steam boilers. From these results he concluded that the caustic solutions would have to be concentrated before attacking the steel in boilers, and conducted experiments to determine whether or not the solutions would concentrate in the small crevices in the seams. He used capillary tubes sealed at one end and connected at the open end to larger tubes. Solutions of about one gram per liter of different salts were put into the tubes. The volume of solution in the capillary part was extremely small in comparison with that in the larger tubes. The capillary was heated, thus vaporizing the liquid in the capillary. The small amount of the liquid in the capillary adhered to the walls and on vaporizing left a small amount of the salt on the walls. When the capillary was cooled the liquid from the larger tube forced its way into it. After the heating and cooling had been repeated a great many times the solution in the capillary slowly became concentrated, while the solution in contact with it, but in the larger tube, remained practically the same as at the start. By means of this procedure Berl caused the solutions in the capillary to reach their saturation point with the subsequent precipitation of the salt from solution, without producing concentration of the solution in the larger tube. He then proceeded to show that the seams in steam boilers have numerous

*Forschungsarbeiten Verein Deutscher Ingenieurewessens, Hefte 295, 1927.

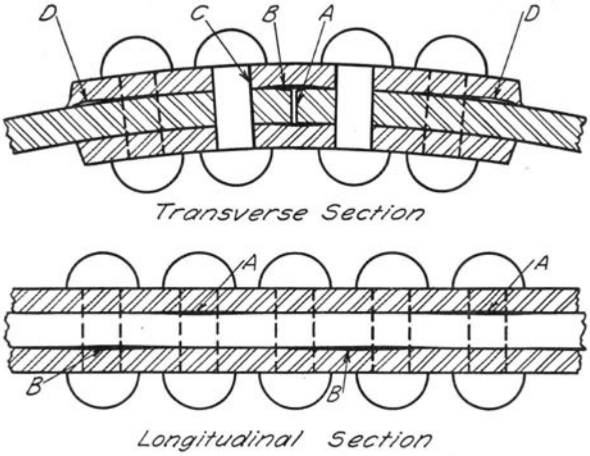

FIG. 22. SECTIONS THROUGH BUTT SEAM SHOWING POINTS OF POSSIBLE CONCENTRATION

capillary spaces in which the solutions could be concentrated in this manner. The raising and lowering of the steam pressure, the heating and cooling of the boiler, etc., all tend to favor slow concentration in these capillary spaces.

In these experiments diffusion was reduced to a minimum. If in addition the solution reacts with the steel as caustic solutions do the chemical reaction itself would cause an increase in concentration when full circulation was lacking. If a small leak should exist the possibility of concentration increases. All these considerations indicate that an increase of concentration within the seam can take place to a sufficient degree to cause embrittlement. Figure 21 shows a section of an embrittled seam illustrating the points of possible concentration in a heavily calked seam. Figure 22 shows in an exaggerated manner these points of possible concentration. Figure 23 shows an embrittled seam with the strap removed. The places where the solution has penetrated between the plates are clearly shown. Some of the deposit left by the solution is still on the plates.

The attention of the investigation was recently called to a large central power plant operating at a pressure of 225 lb. per sq. in. using only 8 per cent makeup of zeolite-treated river water. The ratio of the alkalinity as sodium carbonate to sodium sulphate was 6 to 1 instead of about 1 to 3. An examination of the boiler water showed that the percentage of hydroxide was about 3 times that of the carbonate,

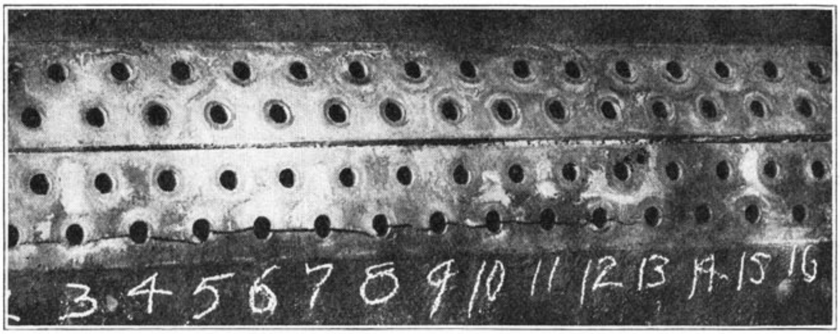

FIG. 23. EMBRITTLED SEAM WITH STRAP REMOVED TO SHOW POINTS OF POSSIBLE CONCENTRATION AND SALT DEPOSITS

which is a condition common to boilers using this type of water at this pressure. When these boilers were down for inspection snowlike salt slowly formed on the inside of the drum where the plates and straps met. When this was scraped off new salt slowly formed. Tests showed this salt to be sodium carbonate. This indicated that the seams undoubtedly contained a concentrated solution of the boiler water high in hydroxide which was slowly seeping out, and when in contact with the carbon dioxide in the air formed the snow-like carbonate. It was estimated that at least two or three grams of this material was removed from a section of the seam only a few feet in length. Taking the maximum concentration reached in the boiler into account it was calculated that it would require about three liters of boiler water to give this amount of salt. It appears highly improbable, since this boiler is of recent design and manufacture, that this volume could exist in the seam; consequently, the only conclusion to be drawn is that the solution seeping out of the seam was much more concentrated than the boiler water ever had been. At the time of inspection the boiler had not given sufficient indication of trouble to justify the expense of a thorough examination from embrittlement cracking. It is being continued in operation under strict supervision.

The production of intercrystalline cracking in steel free from the action of caustic solutions is interesting, and should not be forgotten. It is known that under certain conditions of corrosion and stress nonferrous metals fail by intercrystalline corrosion. It is not unreasonable to presume that certain conditions of strain and corrosion will bring about intercrystalline weakness in boiler plate. The heating of steel in air at high temperatures (burning) causes an intercrystalline weak-

ness. Strained steel in contact with certain molten metals fails by intercrystalline weakness, boiler plate has cracked in riveted areas of nitrate evaporators, etc. All these facts indicate that this type of failure can be produced in various ways by corrosion or attack of the grain boundaries.

If the mere occurrence of intercrystalline failure in a boiler were the only evidence available it would not be right to conclude that it was due to caustic merely because caustic produces such a crack in steel. But when in the hundreds of instances of this type of failure occurring in the United States it is shown that the only factor common to all the boilers affected is the presence of sodium hydroxide in the boiler water and when it is shown that sodium hydroxide alone of all the chemicals encountered in the boiler water will crack steel in this manner, is it not logical to conclude that caustic soda was the contributing agent? Furthermore, it has been shown, both in plant and laboratory, that when the caustic action is prevented by the presence of sulphates, the embrittling action stops.

Before the presence of sodium hydroxide should be accepted finally as the contributing agent in these embrittlement failures and the conclusions reached that all feed waters containing carbonate of soda without the presence of the required amount of sulphates should be treated to counteract the embrittling action, another question remains to be answered. This is, "why have some boilers operated on alkaline waters of this type for years without failure?" An attempt was made to investigate all available plants apparently operating successfully under these conditions. The first case examined was that of a local power plant using alkaline well water. The boilers were over seven years old and operated at a pressure of 160 lb. per sq. in. Analyses of the boiler water indicated that the A. S. M. E. recommended ratio had not been met. The hydroxide formed readily in the boiler. No reason for the lack of failure could be suggested. Six months later, however, the boilers in this plant were found to be badly embrittled. This leads one to conclude that, in default of evidence to the contrary, all boilers operating on this type of feed water, whether natural or produced as the result of water treatment, are in potential danger of embrittlement.

Recently two boiler plants were investigated which used a feed water containing about 12 grains per U. S. gallon of sodium carbonate and no sulphate. These plants operated at a pressure of about 125 lb. per sq. in. with a high makeup and a high rating. The percentage of sodium carbonate in the boiler waters was always at least three times,

and in many cases as high as ten and fifteen times, that of hydroxide. The blow down was frequent and the makeup carried in a large amount of carbonate. The only conclusion to be reached in these cases was that the decomposition of the carbonate had been retarded by the high partial pressure of the carbon dioxide and enough hydroxide had never formed to be detrimental.

Summing up all the evidence placed at the disposal of the investigation and correlating it with the results of the laboratory research it appears evident that the cases referred to as embrittlement have been brought about by the use of water high in sodium carbonate and in which the sodium sulphate was correspondingly low.

20. *Methods of Inhibiting Embrittlement.*—The inhibition of embrittlement apparently may be accomplished by the following methods:

(1) The removal of highly concentrated stresses

(2) The removal of points of possible concentration in seams

(3) Proper treatment of the feed water

The complete avoidance of highly concentrated stresses may be accomplished in the future, but such stresses are inherent in all boilers as at present made, due to methods of design, construction, and operation. Much has been done in recent years toward the manufacturing of seams which are well laid up, the proper alignment of rivet holes, the use of ground rivets, the control of riveting pressures, etc. These improvements all tend toward a decrease in localized stresses, but as long as riveting is used in manufacture, high stresses are almost certain to occur. Naturally, poor workmanship contributes to the occurrence of high localized stresses and all possible effort should be directed towards keeping the stresses as low as is consistent with the production of tight serviceable seams.

The removal of points of possible concentration in the seam is being accomplished to a large degree in new boilers used at higher pressures. Seams are laid up with an almost unbelievable degree of accuracy. The use of inside calking, by newly developed calking machines, and the leaving of the outside seams open, permits detection of a leak and decreases the possibility of concentration in the seams.

Improved methods of boiler design and construction will undoubtedly go a long way toward decreasing the possibility of the occurrence of embrittlement, but at present they are only applicable to boilers for higher pressures and large installations. In smaller boilers built for lower pressures the attention and grade of workmanship necessary for the making of these improved seams cannot be used without exceeding a reasonable cost. Furthermore, this would mean

that the plant using a water not potentially embrittling would have to pay for protection necessary only for plants in which there is possibility of embrittlement. Another fact to be considered is that boilers now in use cannot be changed, but should operate their rated lifetime. The only means of protecting old boilers and making new ones doubly safe against embrittlement is by treatment of the feed water so as to counteract the embrittling effect of the caustic.

The proper treatment to use depends entirely upon the type of feed water and the boiler pressure. If a natural sodium carbonate water is being used and the sulphate content is low, it may be made to meet the A. S. M. E. sulphate ratio by means of sulphate treatment. If settling tanks are available, a lime treatment, followed by the closely controlled addition of aluminum sulphate, iron sulphate, or sulphuric acid, can be used. The use of the sulphates or sulphuric acid should be begun only under the advice of a chemical engineer familiar with this phase of water treatment and frequent analyses should be made to see that the treatment is correct.

If the water contains sodium carbonate as the result of treatment with either soda ash or zeolite, the sulphate treatment may also be used. Equipment is available for adding sulphuric acid in a continuous system, and can be installed at a relatively small cost.

For higher steam pressures it is hard to maintain the sulphate ratio when calcium salts are in the boiler without causing the deposition of sulphate scale; also, in small low-pressure installations, where the supervision of qualified chemists is not available, the sulphate treatment cannot readily be used. In installations of these types the use of phosphates* or tannates is to be recommended. The phosphate, to be effective, must be fed in sufficient amount to react with the calcium and magnesium salts and remain in sufficient amount to maintain a definite ratio with the sodium alkalinity, expressed as sodium carbonate. Likewise enough tannate must be fed to remain in excess of a given amount in the boiler. Each chemical has its own particular field, and should be used only after consulting with someone who understands this phase of water treatment.

For evaporators using alkaline water the use of phosphate has decided advantages. The amounts to be added are comparatively small and will not appreciably increase the total solids. The phosphate removes hardness resulting from condenser leakage and keeps a boiler free from scale.

*A U. S. patent has recently been issued covering the use of sodium phosphate in the conditioning of boiler waters.

21. *Mechanism of Laboratory Embrittlement.*—The results obtained in the laboratory investigation are in accord with the ideas expressed in Bulletin No. 155. The steel has a definite electromotive force with respect to the sodium hydroxide. If this e. m. f. is sufficiently high the iron is attacked with the evolution of hydrogen and the formation of a coating of Fe_3O_4 (magnetic oxide) on the steel. The e. m. f. of steel coated with this oxide is low with respect to the caustic solution, but the fresh metal under the coating has a high e. m. f. towards the solution, a condition which favors penetration. The steel under strain has the grain boundaries under high stress, a condition which adds to the already more chemically active property and accelerates penetration at these points.

That the cracking is the result of an e. m. f. between the steel and the solution is borne out by the results of various tests conducted. First, an increase in temperature causes an increase in the e. m. f. of the metal to the solution and consequently lowers the concentration necessary. Second, any salt which will destroy this e. m. f., such as chromate, when introduced, stops the cracking. Third, if the concentration is raised hydrogen is generated freely and the cracking is stopped since the action is no longer selective due to too high an e. m. f. which favors general attack. Fourth, the time rate can be varied by using a container which has had the oxide coating removed, thus changing the e. m. f. of the specimen with respect to the container.

From all the data available the following very brief and undoubtedly incomplete explanation is offered to account for this particular type of cracking.

The main essential is a solution which has an e. m. f. with respect to steel just sufficient to favor the reaction.

$$3Fe + 4\ OH = Fe_3O_4 + 4\ H$$

The e. m. f. must not be any higher than necessary to start this reaction at the temperature involved. When the metal is in an unstrained condition, a thin compact coat of oxide is formed which is slowly penetrated with the formation of a heavier coat, and eventually the entire metal will be changed to oxide. The attack is fairly even and penetrates the metal at an even rate at all points. If the metal is subjected to sufficient stress under these conditions the grain boundaries become active, first from the increased chemical activity brought about through the energy stored up there by the stress, and second, by an increased e. m. f. produced at these points of high stress. If the

e. m. f. is just sufficient to favor the action on the metal, this slight increase at the grain boundaries becomes sufficient to favor a much more rapid penetration at these points. The products of the action Fe_3O_4 and H_2 both tend to favor further penetration. As already pointed out by Williams and Homerberg, the cathodic hydrogen will penetrate into the fine capillaries at the grain boundaries and reduce any oxides, with the formation of water and an increase in volume, thus increasing the stresses present at the boundaries. This product of chemical action does not plug the crevices and stop further chemical action, but, due to its e. m. f. relation to the solution and the fresh metal inside, acts as a stimulating agent and increases the action at these points.

If the e. m. f. is high, such as produced by the action of an acid on a metal, the generation of H_2 is general and any slight difference in activity between the grains and the boundaries becomes negligible in the excess of e. m. f. produced by the acid. When too concentrated a solution of caustic is used at higher temperatures the test specimen is generally corroded, and even when under strain does not crack. Thus the attack has been so general and vigorous that the influence of the small grain boundary effect is lost.

The retarding influence of sodium sulphate is easily explainable on this basis. The salt crystallizing out forms a saturated solution on the immediate surface of the metal, lowers the e. m. f. of the metal, and stops the action. It is not a plugging effect, as some have suggested, thus keeping the solution away, but, instead, the salt plays the rôle of a buffer solution, lowering the e. m. f. Any oxidizing solution like chromate will produce this effect. The phosphates, acetates, and tannates all act as buffers and keep the e. m. f. too low for the action to take place.

22. *Subjects for Further Investigations.*—Much remains to be done in the detection of new inhibitants and the study of the application of inhibiting agents to boiler water treatment.

A further study of the cracking of boiler plate under repeated stresses and caustic attack would serve to show if the stress at which attack starts can be lowered below the yield point.

A detailed study of the real mechanism of embrittlement cracking is necessary in order to understand the reaction which takes place between the stressed metal and the caustic solution.

VIII. Conclusions

23. *Summary of Conclusions.*—The general conclusions to be drawn from the results obtained in the investigation may be summarized as follows:

(1) Embrittlement in boiler plate is caused by the combined action of stress and chemical attack. The stresses are inherent in the construction and operation of the boiler, while the chemical attack is caused by the presence of sodium hydroxide in the boiler water.

(2) Certain methods of water treatment tend to convert some safe waters into the characteristic type which produces embrittlement.

(3) The presence of sodium sulphate in the feed water tends to retard the embrittling effect of sodium carbonate feed waters, and, if in proper proportions, will stop it entirely.

(4) The presence of phosphates, tannates, chromates, acetates, etc., will also inhibit the embrittling action of caustic soda if these salts are present in the boiler water in proper amounts.

(5) Methods for the introduction of these inhibiting agents to feed waters have been worked out and are in operation in large power plants.

(6) No steel suitable for boiler plate has been found which is resistant to the embrittling action of caustic soda.

APPENDIX A

Bibliography

Bulletin No. 94 of the Engineering Experiment Station, University of Illinois, entitled "The Embrittling Action of Sodium Hydroxide on Soft Steel," issued in 1917, contains a summary of the work conducted on this subject up to and including 1916.

C. E. Stromeyer (The Eng. 124, p. 496, 1917) studied the effect of caustic liquors on steel plate under compression and tension, and found that the metal under tension was brittle on subsequent bending while the metal under compression was not affected.

Dr. E. B. Wolff (Holland) (The Eng. 124, p. 456, 1917) investigated failures in marine boilers in which the cracks were typical of embrittlement. The chemical and physical properties of the steel were such as to meet the specifications. Wolff said the evidence pointed to a peculiar form of destruction of surface layers of otherwise very plastic material, and thought that this might be due to deformation during boring. He was not able to reproduce similar cracks in holes bored with a blunt drill or with excessive stress at the point of contact with the rivet, by slipping of the plates, or by the fatigue produced by heating and cooling. No study of water conditions was made.

Walter Rosenhain and D. Hansen (Jour. Iron and Steel Inst. 11, p. 24, 1920) investigated several cases of cracked boiler plates similar to the embrittlement type and could find no general chemical or physical defects in the metal. The cracks were intercrystalline in nature. The investigators tried to develop similar cracks by prolonged stresses but were not successful. They suggest that this type of crack may be produced by stresses acting over a period of years. In their discussion they state that corrosion or chemical action may accelerate intercrystalline cracking, and point out that in the cases investigated corrosive influences had been at work, and may have accelerated the formation of the crack. No study was made of the water used.

Cecil Desch, in a paper on chemical influences in the failure of metals under stress (Eng'g. 111, p. 418, 1921), states that chemical action frequently advances more rapidly along the surfaces which separate the crystal grains than through the mass of the metal, and is more likely to occur when the portion exposed to the reagent is in a state of tension than when it is in an unstrained condition. Strong acids are not selective. Passages of gases into the metals appear to follow the boundaries and the same may be said of some weak electrolytes.

J. A. Jones, Research Department, Woolwich Arsenal, England (Trans. Farady Soc., 17, p. 102, 1921), in investigating the failure of pans used in evaporating nitrates found the cracks to be of the embrittlement nature and was able to reproduce these cracks by means of combining stress with the chemical action of various nitrate solutions. In a limited number of cases he produced intercrystalline cracks by using potassium hydroxide solution. He concluded that these cracks occur only when the stress is above a certain value, and is combined with chemical action.

H. J. French (Chem. and Met. Eng., 24, p. 1207, 1922) studied the effect of elevated temperature on boiler plate and found an increase in the tensile strength up to 290 deg. C. (550 deg. F.) followed by a decrease. The normal strength was reached again at 370 deg. C. (700 deg. F.). At higher temperatures the strength decreased very rapidly.

R. S. Williams and V. O. Homerberg (Trans. Amer. Soc. Steel Treating, April, 1924) studied intercrystalline fracture in steel, and concluded that the impurities are located around the grain boundaries and are attacked by the action of hydrogen and hot caustic solutions. This action is accelerated by stress.

L. R. Gray (Report of Prime Movers Committee N. E. L. A., 1926) described the system of sulphuric acid treatment used on natural sodium carbonate water at Dallas, Texas. The same publication contains a description of the embrittlement encountered by the Southern California Edison Co. as well as statements by the Babcock and Wilcox Co. and the Permutit Co. relative to embrittlement of boiler plate.

C. E. Stromeyer (Memorandum by Chief Engineer for the year 1925, Manchester Steam User's Association) in summing up the cases of boiler failures which have come to his attention in England, shows that a large number of cases of embrittlement attributed to other causes than caustic in the water are now readily seen to be due to caustic. He told of testing pieces of steel subjected to tension in caustic evaporators and reported that they became brittle in a few months. The concentration of caustic solution was between 200 and 500 grams per liter.

During September 1925 the Association of Large Boiler Owners, of Germany, held a session at Darmstadt and discussed the effect of boiler manufacture and feed water. The proceedings were published in a book called "Speisewasserpflege" (Boiler feed water treatment) published by the Association of Large Boiler Owners, Berlin, 1926.

At this meeting Prof. R. Baumann of Stuttgart reported his experience with intercrystalline cracking in caustic concentrators, and showed that the cracking occurred in parts under stress and in contact with caustic solutions. Chief Engineer Ries of Munich reported that he had been "able to prove that damage takes place only at such points which have been worked in one way or another be it through riveting, drilling, fitting, cutting of threads, etc., or which have been stressed in some manner; and which come into contact with caustic soda solution." Prof. A. Thiel of Marburg discussed the possibility of caustic concentrating in the seams of boilers and showed that if this were possible the steel would become embrittled. He compared seams to capillaries and said sodium hydroxide would concentrate to 77.5 per cent NaOH at 200 deg. C. No experimental data were given to support these figures. He stated further that concentrated sodium hydroxide attacked steel to form hydrogen, and the hydrogen embrittled the steel. H. Kreigsheim commented on the sulphate-carbonate ratio as suggested in the United States by the A. S. M. E. code committee. He presented experimental data from tests run at Columbia University to show that steel which was cracked in contact with hydrogen electrically generated in caustic solutions as well as with caustic and sulphate solutions, cracked in a transcrystalline manner. He tried to show that hydrogen brittleness was transcrystalline.

F. Korber and A. Pomp in their paper "Rissbildungen und Anfressungen auf Dampfkesselelementen" (Cracking and Corrosion of Steam Boiler parts) (Zeitschrift des Bayerischen Revisions—Vereins, Dec. 15, 1926, pp. 279, 301) discussed cracking in boilers. The cracking consisted entirely of that encountered in bent or strained parts in direct contact with the boiler water. The cracks were all corrosion cracks. He showed the presence of lines of stress and how the corrosion followed the lines of stress.

Dr. Ing. Fry (The Behavior of Materials used in Boiler Construction when Subjected to Service Conditions) (Kruppsche Monatschefte, Vol. 7, Nov. 1926, pp. 185-196) reported a new type of steel called "Izett" which did not age after cold work. This steel could be cold worked and still have a high impact value. The older boiler steel would lose its impact strength after cold work. His theory for the use of this steel was that boiler plate is cold worked and highly stressed and then reheated to around 200 deg. C. which lowers the impact value of the steel. A steel of low impact value would crack more easily; consequently, he concluded that the service cracks encountered in boilers are due to the aged steel. He also made the state-

ment that the new steel would not become embrittled under steam and caustic attack and showed the results of tests where the new steel did not crack in caustic solution. (The results of tests conducted at the University of Illinois on this steel showed that it was not any more resistant to embrittlement than regular American boiler plate.)

Dr. Fry also reported a method of etching to bring out strain configurations in steel. His results in this respect confirm similar work done in various laboratories toward developing methods of detecting the effect of localized stresses.

Prof. R. Baumann ("Zur Sicherheit des Dampfkesselbetriebes," edited by the Union of Large Steam Boiler Users, published by Julius Springer, Berlin, 1927) has reported the results of his research to determine the possibility of concentration of solutions in seams. He showed definite concentration in pockets or seams built into test containers, even where there was the possibility of diffusion. His results showed that leaky seams caused the concentration to take place at a more rapid rate.

E. Berl ("Untersuchungen über die Einwirkung von Laugen und Verschiedenen Salzen auf Eisen," Forschungsarbeiten auf dem Gebiete des Ingenieurewessens, Heft 295, 1927) investigated the action of different salt solutions on iron at pressures up to 250 atmospheres. The results show that iron was not appreciably attacked by sodium hydroxide at the concentration occuring in the boiler, i.e., up to 5 grams per liter (about 300 grains per gallon) even at pressures of 50 atmospheres. When the caustic concentration reached 100 grams per liter the action was very active. The ductility of unstressed iron was also reduced. Berl compared the seams to capillaries, and he demonstrated that dilute solutions of salts could be concentrated to their saturation point by heating and cooling capillaries filled with a dilute solution in contact with a larger body of dilute solution. A glass tube was drawn out to a capillary at one end and enlarged at the other end. The end of the capillary was sealed and dilute solutions of various salts put in the tube. On the tube being held with the enlarged portion up and the capillary being heated the solution in the capillary formed steam and condensed in the larger volume of solution in the large portion of the tube. Part of the salt remained behind on the inner surface of the capillary. On subsequent cooling the solution flowed back into the capillary. The salt remaining caused the solution to become stronger. After many heatings and coolings the solution in the capillary became saturated while the solution in the larger portion was still dilute. He showed that in capillaries, diffusion, which

entered into Baumann's tests and kept the concentration down, becomes almost negligible. He showed further that sodium sulphate in the ratios recommended in the United States for stopping embrittlement retards the action of even concentrated solutions of caustic.

R. E. Hall ("A Physico-Chemical Study of Scale Formation and Boiler-Water Conditioning," Bulletin 24, Mining and Metallurgical Investigations, Carnegie Institute of Technology, 1927) and his co-workers conducted a series of tests to explain scale formation from a physical-chemical viewpoint. He shows that a certain ratio of carbonate to sulphate ions must exist to prevent sulphate scale in the presence of calcium. This depends upon the steam pressure. He also states that a phosphate-sulphate ratio is more effective and less subject to the difficulty encountered by the decomposition of the carbonate. The results of his experiments indicate that organic materials apparently influence the end points of the regular methyl orange titration so that the reported carbonate is erroneous. He shows that the organic matter does not stop the decomposition of the carbonate but merely affects the end point with methyl orange as an indicator.

D. T. McAdam, Jr. ("Stress-Strain Cycle Relationship and Corrosion Fatigue of Metals," Proc. A. S. T. M., Vol. 26, 1926, p. 269) reported the results of a series of corrosion fatigue tests, and showed that corrosion accelerated fatigue and lowered the endurance limit. In discussing the failures he said, "their chief progress is probably along intercrystalline boundaries. Preliminary investigation of ingot iron indicates that for this material, corrosion fatigue failure is at least partly intercrystalline." In his discussion he said "Microscopic examination of failed corrosion-fatigue specimens of a variety of steels has not revealed any purely intercrystalline fracture. In its path from one inclusion to another, however, a crack sometimes deviates and for a short distance follows intercrystalline boundaries." This substantiates the information given by F. F. Lucas ("Observations on the Microstructure of the Path of Fatigue Failure in a Specimen of Armco Iron," Trans. Amer. Soc. Steel Treating, Vol. 11, 1927, p. 540) who concluded that grain boundaries do not appear to be a potential source of weakness.

H. S. Rawdon ("The Intercrystalline Corrosion of Metals," Indus. and Eng. Chem., Vol. 19, No. 5, pp. 613-619, 1927) concludes that "The corrosion of a metal while under tensile stress is a common cause of intercrystalline brittleness although even here it is only by means of certain corrosive solutions, which are different for the different metals, that the result is accomplished.

In general, any practical remedy for the trouble must be along one of two lines. The stress acting on the metal, whether internally or externally applied, may be reduced considerably below the yield point. Most of the short-time laboratory tests have shown that in order to produce failure within a reasonable time in the laboratory the metal must be stressed close to its yield point. The practical solution of the problem of corrosion cracking in rough brasses and other copper alloys has been along this line. The other method is to reduce the corrosion attack either by protective coatings, as in the case of duralumin, or by the preventing so far as possible the formation and accumulation of the corrosive solutions, as in the treatment for the prevention of caustic embrittlement." He states further, "While recognizing that the two factors, tensile stress and corrosion, are equally important in the failure of boiler steel by intercrystalline embrittlement, Parr and Straub have emphasized the importance of controlling the latter factor as being the only practical remedy. On the other hand, German investigators have minimized or discounted entirely the corrosive attack and emphasized the importance of the results of the stressed condition upon the mechanical properties of the steel (Baumann, Fry). It has been shown that the cold-working of the steel by pounding, riveting, and any other cold-working operations, followed by reheating at a relatively low temperature (200° C.) reduces the shock resistance of mild steel enormously—for example in the ratio of 25 to 3. Such a condition is in itself a grave source of danger and is not to be lightly passed over; however, its connection with embrittlement resulting from intercrystalline corrosion, the existence of which has been definitely established by experiment, has not been made clear."

A. H. White and T. H. Walker (American Water Works Association, 1927) reported on the acid treatment of zeolite-treated water in the Beacon Street heating plant of the Detroit Edison Co. They gave the results of using sulphuric acid and sulphuric with phosphoric acid. The use of the latter acid allowed them to neutralize more sodium carbonate and reduce the carbon dioxide in the steam.

APPENDIX B

Embrittlement at the University of Illinois Power Plant

The University of Illinois in the early days used steam boilers for heating alone. The condensate was returned to the boilers. After about 35 or 40 years, during which no difficulty of the embrittlement type was encountered, the University power house was enlarged so as to generate power. This resulted in the concentration increasing in the boilers due to the fact that the exhaust steam was not returned to the boiler. Shortly after this embrittlement started to manifest itself.

The official record of the occurrence of this type of difficulty in the Universtiy of Illinois boilers dates back to 1910. The boilers operating were as follows:

Nos. 1, 2, 5, 6,	Babcock & Wilcox
3, 7, 8,	Stirling
4	National

They were from 6 to 15 years of age—the Stirling boilers being the newer ones.

The inspectors' reports indicate that difficulties as listed below were noted at the stated times:

July, 1910—Boilers No. 4 and 5. Internally clean. Cracks in plate at corners of cross box in south drum of No. 5. One cracked header on rear end No. 4 and leakage noted at one rear circulator and one girth seam on each drum.

Dec. 1912—The top middle drum No. 7 boiler has been replaced with a new one. (Old one installed 1904.) No. 3 boiler cracked ligament in tube sheet in bottom drum, several tube ends leaking. No. 6 The fifth rear header is cracked, should be renewed before boiler is used. One rear circulator and mud drum nipple leaking. (During this time several blow off flanges cracked and had to be replaced.)

In 1911 a new boiler plant was put in operation using two Babcock & Wilcox boilers operating at a pressure of 140 lb. per sq. in. This plant was to furnish power in addition to steam. The older plant was still kept in service for heating purposes. The inspectors' reports continue as follows:

Dec. 1912—Boilers No. 1 and 2. New plant considerable leakage at girth seams should be caulked.

July, 1913—Boilers No. 1 and 2. New plant girth seams still leaking.

April, 1914—Boilers No. 1 and 2. New plant bad leaking at girth seams.

March, 1915—Cracking between rivets on drums in new plant. Advise replacing.

May, 1915—Old power plant—Boiler No. 1—Leaks between two rivets in front girth seam. Three leaky rivets in rear cross box.

No. 2—Leaky rivets in front cross box.
No. 3—Cracked plate bottom drum.
Leaky joint middle top drum.
Blow-off flange cracked and pieces of plate cracked off.
No. 4—Renew six tubes.
No. 5 and 6—Out of service.
No. 7—Lap seam leaking bottom drum.
No. 8—Leak top middle drum.

In 1914 two new Babcock & Wilcox boilers (Nos. 3 and 4) had been installed in the new power plant.

In commenting on the difficulty being experienced at the University of Illinois power plants the report of the Insurance and Inspection Company read as follows:

March 20, 1915—From our experience with the water used in your locality, it is evident to our mind that the cracks have started at all points where leaks have developed on these seams. This would mean that we consider that the girth seams as described in the drums of No. 1 boiler opposite where leakage had been shown, are fractured, and it would be only a short time before the drums would have to be taken out of commission and replaced with new ones.

Wherever we have made any repairs to seams of this kind we have always found the cracks to extend considerably beyond the points where they could be noted before the plate was cut out. Therefore, we strongly advise and recommend that all four drums of these boilers be abandoned and replaced with new ones.

In regard to the feed water used in operation of these boilers, it has been admitted that this brings about a change in the condition of the plates, which later develops into fractures.

When the difficulty became apparent in 1912, and it was noted that similar cracking had occurred in other plants using water of a type similar to that used at the University, attempts were made to treat the water to neutralize the effect of the caustic alkalinity. A letter written July 11, 1913 reads as follows:

Mr. H. D. Oberdorfer

114 Engineering Hall.

Dear Sir:—The investigation on brittleness of boiler plates has been reported on so far as our experiments here are concerned, and cover the time up to the first of July. I can say that all our experiences so far are in accord with the report of the Superintendent for the Babcock and Wilcox Company, which is returned herewith.

The effect of sodium hydrate can be neutralized by any salt which will react with that substance to form a new compound which will not hydrolize in the boiler. Magnesium sulfate is a good material to use for this purpose. The only point to be guarded is an excess of the material over the chemical equivalent necessary to neutralize the sodium hydrate.

Since magnesium salts are corroding it is necessary to avoid an excess of this reagent. However, this is a matter easily controlled and I would endorse the recommendation under proper observations as indicated. Very truly yours

S. W. Parr

Prof. of Applied Chemistry.

Early in 1915 the suggestion was made to add sulphuric acid to neutralize the sodium carbonate in the feed water. Under the date of July 15, 1915, Mr. I. Harter, Jr., then superintendent of the Babcock & Wilcox Co., wrote to Prof. C. R. Richards, then Acting Dean of the College of Engineering, as follows:

I have your letter of July 12th stating that Prof. Parr has recommended the elimination of the sodium carbonate present in the feed water by treatment with sulfuric acid.

I do not feel that the sulfuric acid method will in practice be satisfactory. I am assuming of course, that the treatment will be external to the boiler so that the formation of CO_2 will not result in its being carried into the boiler itself, and I am also assuming that the treatment will be checked by continual titrations, so that by no possibility can any free acid go over into the boiler.

On Feb. 10, 1916, Mr. W. L. Abbott wrote to Prof. S. W. Parr in regard to the proposed acid treatment.

I thank you for your letter of Feb. 7th with attached charts descriptive of the results obtained in reducing the alkalinity of the water in the boilers by feeding the boilers with magnesium sulfate.

I note your suggestion to substitute sulfuric acid for magnesium sulfate. This is a proposition which a chemist would naturally make and from which a boiler user would naturally shrink; not that the results would not be exactly as you predict so long as the treatment is wisely administered, but rather as to what the results might be if the treatment is bungled. On the whole, I would like to see the acid treatment tried out, provided it can be arranged for in a way which will reasonably preclude the possibility of damage to the boiler or piping by contact with acid of considerable strength.

About March, 1916 the use of sulphuric acid to partially neutralize the sodium carbonate was substituted for that of magnesium sulphate which had been used since early in 1914. This treatment was carried on in two 40 000 gallon tanks under close chemical supervision. This treatment has been continued and is still in use. After 10 years of operation the boilers were thoroughly examined, test rivets removed, holes cleaned, etc., and no indication of embrittlement or corrosion was evident. The boilers were free from leaks.

A few abbreviated reports of the insurance inspectors in regard to the results of inspection of boilers in the new plant are given below

to indicate the change brought about in the boilers after the sulphate treatment was started. These, when compared with the reports issued previous to treatment, clearly show the results of the treatment.

	Internally		*Externally*	
Nov. 1918	#4 Boiler	light scale	#1, 2, 3, 4	good order
Sept. 1919	#1, 2, 3, 4	good order	#1, 2, 3, 4	good order
Sept. 1921	#1, 2, 3, 4, 5, 6	good order	#1, 2, 3, 4, 5, 6	good order
Aug. 1922	#1, 2, 3, 4, 5, 6	good order	#1, 2, 3, 4, 5, 6	good order
Sept. 1923	#5, 6	light scale	#1, 2, 3, 4, 5, 6	good order
Oct. 1924	#3, 4	light scale	#1, 2, 3, 4, 5, 6	good order
Oct. 1925	#1, 2, 3, 4, 5, 6	light scale	#1, 2, 3, 4, 5, 6	good order
Mar. 1926	#1, 2, 3, 4, 5, 6	light scale	#1, 2, 3, 4, 5, 6	good order

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